Vol. XXVI. [DECEMBER, 1904.] No. 12.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

ON THE FUNDAMENTAL CONCEPTIONS UNDERLYING THE CHEMISTRY OF THE ELEMENT CARBON.[1]

BY J. U. NEF.

Received September 28, 1904.

Two fundamental conceptions underlie our present system of carbon chemistry. First, the idea of the constant quadrivalence of carbon, which explains most adequately the existence of the vast array of carbon compounds. Second, the conception of substitution or metalepsis which gives us a basis for interpreting many of the reactions shown by these substances.

These ideas are, however, in the light of investigations of the past twenty years, inadequate; they must be replaced by the conception of a variable valence of carbon and by the conception of dissociation in its broadest sense.

A rigid application of the latter conceptions gives a far simpler basis for interpreting all the reactions of carbon chemistry; they are naturally also applicable to the chemistry of all the other elements.

I. ON THE VALENCE OF THE CARBON ATOM.

The progress of organic chemistry since 1858 is due chiefly to the development of a few very simple ideas concerning the valence

[1] Presented before the International Congress of Arts and Science, at St. Louis, September 20, 1904.

of the elements, ideas which were first clearly and fully presented at that time by Kekulé.

Hydrogen, oxygen and nitrogen are the elements which most frequently combine with carbon to form the so-called organic compounds. Since the compounds of one atom of oxygen, nitrogen, or carbon with hydrogen possess the empirical formulae, $O{=}H_2$, $N{\equiv}H_3$, $C{\equiv}H_4$, the conception naturally presents itself that the capacity of the various elements for holding hydrogen atoms varies. Oxygen is capable of holding two such atoms, nitrogen holds three, and carbon four atoms of hydrogen. Therefore we assume, taking hydrogen as our unit, that the valence of the element oxygen is two, —O—, of nitrogen, three, $-\overset{|}{\underset{|}{N}}-$, and of carbon, four, $-\overset{|}{\underset{|}{\overset{|}{\underset{|}{C}}}}-$. Without going into much detail concerning the nature of the valence, or what is the same thing concerning the nature of the forces inherent in our atoms, we assume briefly that every atom of an element possesses one, two, three, four or more such units of force and we call the element univalent, bivalent, trivalent, quadrivalent, etc., according to the number of such units it possesses. It is by virtue of the existence of these units of force that the compounds made up of the same or of various elementary atoms exist. We assume that in such a molecular compound the atoms are bound one to another in a definite way by means of their affinity units.

Since the development of these ideas concerning the valence of the elements there has been a great deal of work carried on with the object of determining whether the valence of an element is constant or whether it may vary; the majority of chemists are now convinced that it may vary.

The valence of nitrogen may be three or five. The valences of hydrogen, oxygen and carbon, on the other hand, have, until recently, been assumed always to remain constant, *i. e.*, one, two and four, respectively.

Since the complexity, the very great variety and number of existing compounds containing carbon are unquestionably to be attributed to the peculiar nature of the forces inherent in the carbon atom, let us consider a little more in detail what hypotheses we make in our present system of carbon chemistry concerning

this element. We assume first that the valence of the carbon atom is always four; second, that the four valences or affinity units of the carbon atom are equivalent; third, that they are distributed in space in three dimensions and act in the direction of the axes of a tetrahedron; fourth, that the carbon atoms can unite with one another by means of one, two or three affinity units to form what we usually call chains. These chains may be open, or closed rings or cycles. The number of carbon atoms thus bound to one another may be exceedingly large. The closed chains usually contain three, four, five, six or seven carbon atoms in the ring. We may have in these chains, whether open or closed, some of the carbon atoms replaced by oxygen, nitrogen, sulphur or other elements. If now we unite the extra valences of each carbon or other atom—*i. e.*, those affiinity units which are not necessary for binding the atoms together in chains—with other atoms or radicals, it is at once evident that we can represent, theoretically, by so-called graphical formulae, molecules of great complexity.

It is also at once obvious that with a small number of atoms it must be possible to construct a relatively large number of aggregates which differ from one another simply in the way the atoms are bound together. In 1884, for instance, fifty-five totally different substances of the empirical formula $C_9H_{10}O_3$ were actually known. We call them isomers.

One of the chief problems of organic chemistry, since 1858, has been to determine on the basis of these ideas of valence the "constitution" of the carbon compounds. We determine by methods which are called synthetic, as well as by an exhaustive study of the reactions of a given compound, what may be called the "architecture" of its molecule, *i. e.*, we determine how the various atoms of carbon, nitrogen, oxygen, hydrogen, etc., of which the substance may be composed, are joined together by virtue of their affinity units. How much has been accomplished on the basis of these ideas during the past forty-six years and how beautifully and simply all the facts known with regard to the almost countless carbon compounds are thus explained, only those can fully appreciate who have a detailed knowledge of the subject. Notwithstanding the large number of workers in the field, it has often required more than a decade of work to determine

the molecular architecture of one single carbon compound, and the question at times seriously presents itself whether we must not reach our limitations in this respect.

In any case, one point is deserving of especial emphasis: This idea of structure which has been applied chiefly to molecules containing the element carbon attributes to them a rigidity which is improbable from a purely dynamic standpoint.

The present system of organic chemistry is thus founded upon the assumption that the valence of all the atoms of carbon, wherever found, remains invariably four. In the earlier part of the last century many attempts were made to isolate the hydrocarbon methylene, $C{=}H_2$, which must contain bivalent carbon. Dumas and Peligot tried to obtain this substance from methyl alcohol, $H_2C\begin{matrix}H\\OH\end{matrix}$, by loss of water. Perrot tried to isolate it from methyl chloride, $H_2C\begin{matrix}H\\Cl\end{matrix}$, by dissociation into methylene and hydrogen chloride at a high temperature. Berthelot, Butlerow, Wurtz and Kolbe also made many fruitless attempts in this direction. As a final result of these repeated and negative efforts chemists finally became convinced that compounds containing bivalent carbon could not be isolated and the conclusion, therefore, that carbon was one of the few elements possessing a constant valence became very general.

There has, however, long existed one very simple compound of carbon which does not adjust itself to this system—namely, the inactive and poisonous carbon monoxide. If we assume the valence of oxygen as two, then we have here simply a derivative of methylene in which the two hydrogen atoms are substituted by oxygen, $C{=}O$. To be sure, there were many chemists who preferred to consider the valence of carbon in carbon monoxide as four, thus making the valence of oxygen four, $C{\equiv}O$; and when we bear in mind that the other members of the oxygen group, sulphur, selenium and tellurium, exist as di-, tetra- and hexavalent atoms there is some justification for this interpretation. To me, personally, however, it seems in the highest degree improbable that two atoms should be thus bound to each other by four affinity units.

About fourteen years ago a series of systematic experiments was undertaken with the object of ascertaining whether carbon can exist in a bivalent condition. The experiments have established this point in a most decisive manner; we have now quite an array of substances which contain bivalent carbon.

Furthermore, it has been possible to prove, from the experience gained in their study, that methylene chemistry plays an important rôle in many of the simplest reactions of organic chemistry, reactions which have hitherto been explained on the basis of substitution.

At the time when these experiments were undertaken there existed, besides carbon monoxide, several substances which might contain bivalent carbon, namely, prussic acid and its salts, the cyanides, HN=C and M—N=C. Also the so-called carbylamines, RN=C, discovered in 1866 by Gautier. These substances were, therefore, exhaustively studied in order to establish rigidly, by experiment, whether bivalent carbon was present or absent. The presence of dyad carbon in these compounds having been established and its properties thus being known, the problem then presenting itself was the isolation of methylene and its homologues.

You are probably all aware that Gay-Lussac established, in 1815, the existence of a radical, composed of one atom of carbon and one of nitrogen, in prussic acid and the cyanides. This radical, cyanogen, plays in its compounds a rôle similar to that of the elements of the halogen group. In 1832, Pelouse discovered the alkylcyanides, R—C≡N, by treating potassium cyanide with alkyliodides or with alkyl potassium sulphates,

$$KCN + RI \text{ or } ROSO_2OK \rightarrowtail R—C{\equiv}N + KI \text{ or } KOSO_2OK,$$

an apparent double decomposition reaction by which we obtain a compound in which the radical R ($=C_nH_{2n+1}$) is joined to the cyanogen group by means of carbon. The alkylcyanides thus obtained are neutral, pleasant smelling, harmless liquids resembling ether, chloroform and the alkylhaloids, R—Cl, R—Br and RI.

In 1866, Gautier discovered a new class of organic compounds by treating cyanide of silver with alkyliodides,

$$R—I + Ag—(NC) \rightarrowtail AgI + R—N{=}C,$$

a reaction which is apparently a double decomposition reaction. They are isomeric, not identical, with the alkylcyanides of Pelouse. He called them the carbylamines or isonitriles and proved that

the alkyl group is bound to the cyanogen radical by means of nitrogen, RN=C or RN≡C.

It thus became evident that we must distinguish between two cyanogen radicals, namely, one which in its compounds is bound to alkyl hydrogen or metal by means of carbon, R—C≡N, H—C⋮N, M—C⋮N, and another which is joined to these elements, or groups, by means of nitrogen, RN=C, HN:C, MN:C. We may call the former radical cyanogen, —C⋮N, and the latter isocyanogen, —N:C or —N≡C; these radicals may, obviously, combine with each other to form three isomers of the empirical formula, C_2N_2. The substances discovered by Gautier, the alkylisocyanides, RN=C or RN≡C, have properties strikingly different from those of their isomers—the alkylcyanides, R—C≡N, of Pelouse.

They are poisonous, nauseating compounds which affect the throat like prussic acid and color the blood intensely red; they produce violent headaches and vomiting. Their odor is most pronounced and persistent. Hofmann, who, in 1868, discovered another method for making them from primary amines, chloroform and caustic potash,

$$RNH_2 + 3KOH + CHCl_3 \rightarrow R—N=C + 3KCl + 3H_2O,$$

found it impossible to work with them except for very short periods.

An exhaustive study of the reactions of these alkylisocyanides, carried out in 1891-'92, led to the definite conclusion that they contain a dyad carbon atom, *i. e.*, they possess the constitution represented by the formula RN=C; the other possible formula with quadrivalent carbon and quinquivalent nitrogen, R—N≡C, is excluded by the facts.

The alkylisocyanides belong to the vast category of unsaturated compounds whose chemistry will be briefly discussed from a perfectly general standpoint below; they manifest their great chemical activity especially by absorbing other substances, forming new molecules in which the valence of carbon has changed from two to four. Such reactions we call additive. Two molecules simply unite to form one new molecule—the addition product.

A molecule containing an unsaturated carbon atom, *i. e.*, one with two of its valences latent or polarized, RN=C or RN=C can not, *per se*, show any chemical activity whatever.

This is also true of a system containing a pair of doubly or triply bound carbon atoms, ethylene, $CH_2=CH_2$, and acetylene, $HC\equiv CH$; and finally of a saturated system which we may represent by a paraffine, C_nH_{2n+2}, for instance, marsh gas, $H-\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H$.

All these substances manifest chemical activity simply because they are, to a greater or less degree, in a dissociated, or what may be called an active, condition.

A given quantity of alkylisocyanide contains an extremely small per cent. of molecules with two free affinity units, $RN=C<$; these are in dynamic equilibrium with the absolutely inert molecules, $RN=C$, or better, $RN=C^1$. That this percentage varies with the nature and mass of R is shown by the fact that various alkylated and arylated isocyanides manifest different degrees of chemical activity. Carbon monoxide possesses relatively a smaller number of such active particles, $O=C<$, and consequently is a comparatively inert substance, since the speed of addition reactions shown by unsaturated compounds must naturally be directly in proportion to the per cent. of active molecules present. A similar conception obviously explains the relative differences in reactivity shown by the various members of the olefine and acetylene series. Marsh gas, a saturated system, reacts with other substances because it is partially dissociated as follows:

$$CH_4 \rightleftarrows CH_3- + H- \text{ and } H_2C= + 2H.$$

From this point of view chemical action depends entirely upon dissociation processes. The reactions often proceed with very great slowness because the percentage of dissociation is extremely low, possibly 0.1 to 0.001 per cent., or even less.

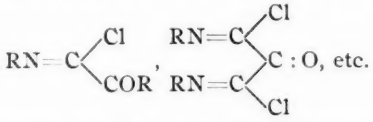
Turning now to a consideration of the reactions of alkylisocyanides, the substances which are absorbed by the unsaturated carbon atom present in the isonitriles are the following:

I. *Halogens* (chlorine, bromine, iodine; speed of reaction in the order named),

$$RN=C< + \underset{|}{X}=\underset{|}{X} \rightarrowtail RN=C\overset{X}{\underset{X}{\overset{\|}{\underset{\|}{C}}}} \rightarrowtail RN=C\overset{X}{\underset{X}{\diagup\!\diagdown}}.$$

The reactions, especially those with chlorine and bromine, take place with great evolution of heat at —20°.

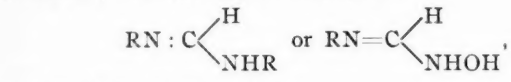
II. *Acid Chlorides,* such as RCO—Cl, Cl—OC_2H_5, Cl—CO—Cl, Cl—CN, Cl—COOR to form the addition products,



A hyphen denotes the point where the compounds are partially dissociated and consequently absorbed. These reactions, especially those with phosgene and ethyl hypochlorite, take place with great violence at —20°.

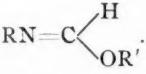
III. *Oxygen and Sulphur,* to form isocyanates and mustard oils, RN=C=O and RN=C=S. Methylisocyanide unites directly at its boiling-point, 58°, with the oxygen of the air. The dry oxides of silver and mercury are reduced to metals with violence at 40°, alykylisocyanate being first formed. This shows the great affinity of bivalent carbon for oxygen.

IV. *Primary Amines and Hydroxylamine,*

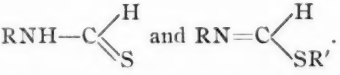


giving amidines of oxyamidines.

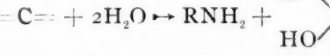
V. *Alcohols,* in the presence of an alkali, are absorbed, giving imido ethers,



VI. *Hydrogen Sulphide and Mercaptans* give readily at 100° the addition products



VII. *Acids.* Aqueous mineral acids act with great violence on the isonitriles, giving primary amines and formic acid,



In the absence of water and on diluting the alkylisocyanides with absolute ether, perfectly dry halogen hydride causes the separation of white hygroscopic salt-like substances of the empirical formula 2RNC, 3HX (X=Cl, Br or I). For this reason Gautier, as well as Hofmann, supposed the isonitriles to be basic compounds, *i. e.,* substances behaving like ammonia—hence the name carbylamine was given them by Gautier. Further study has shown, however, that this conclusion was erroneous. The isonitriles are entirely devoid of basic properties; the great violence with which they react with halogen hydrides is due to the presence of unsaturated carbon. The reaction probably takes place as follows:

$$RN{=}C{<}+H{-}X \rightarrowtail RN{=}C\begin{matrix}H\\X\end{matrix} \quad (I).$$

$$RN{=}C{<}\begin{matrix}H\\+\end{matrix}X{-}C:NR \rightarrowtail RN:\begin{matrix}X\\C\end{matrix}{-}CH:NR \quad (II).$$

$$RN{=}\begin{matrix}X\\C\end{matrix}{-}CH{=}NR + 2H{-}X \rightarrowtail RNH{-}\begin{matrix}X_2\\C\end{matrix}{-}CHX{-}NHR \quad (III).$$

Reversibility of the Reactions.—The most striking property of these addition products of the isonitriles, $RN:C\begin{matrix}X\\Y\end{matrix}$, is their low point of dissociation, *i. e.,* the carbon atom which has absorbed the X-Y thus becoming quadrivalent is unable to hold X Y above certain temperature limits. There is consequently in every case a temperature varying with the nature and mass of X and Y, as well as with the nature and mass of the groups bound to the other two affinity units of carbon, at which the carbon atom becomes spontaneously dyad and is unable to remain in a quadrivalent condition; it was subsequently possible to prove that this is a perfectly general property of this atom.

All the addition products under discussion are partially dissociated,

$$RN:C\begin{matrix}X\\Y\end{matrix} \rightleftarrows RN{=}C{<}+X{-}Y,$$

the dissociation increasing as the temperature is raised— in other words, the valence of carbon at temperatures below the dissocia-

tion point is an equilibrium phenomenon; dynamic equilibrium exists between bivalent and quadrivalent carbon.

The point of complete dissociation of the various addition products of the isonitriles has not yet been accurately determined in every case. The following data with reference to the dissociation points of carbon monoxide addition products are of interest and therefore used for illustration in this connection:

	Dissociation point.
Formaldehyde, $O:C<H_2$,	600°
Formamide, $O=C<\begin{matrix}H\\NH_2\end{matrix}$,	250° (about)
Formic acid, $O=C<\begin{matrix}H\\OH\end{matrix}$,	169°
Formhydroxamic acid, $O=C<\begin{matrix}H\\NHOH\end{matrix}$,	85°
Formylchloride, $O:C<\begin{matrix}H\\Cl\end{matrix}$,	—20° (below)

Since these substances containing quadrivalent carbon decompose spontaneously into carbon monoxide, *i. e.*, can not exist in the quadrivalent condition at temperatures above those indicated, it is self-evident that at lower temperatures the addition products must be partially dissociated and that in the future we must be able to determine, in each case with absolute accuracy, the per cent. of dissociation at any temperature. A striking experiment with formhydroxamic acid, dissociation point 85°, proves the correctness of this conclusion; on allowing this crystalline substance to stand at 20° in acetone solution the following reaction takes place quantitatively:

$$HONH\diagdown\!\!\diagup C=O \rightleftharpoons H-NHOH + =CO + \underset{|}{O}-\underset{|}{C}:(CH_3)_2 \rightarrowtail$$

$$CH_3\diagdown\!\!\diagup C=NOH + H-OH + =CO \rightarrowtail$$

$$(CH_3)_2:C=NOH + \begin{matrix}H\\HO\end{matrix}\!\!\diagdown\!\!\diagup C:O.$$

In a similar manner we can prove that the isonitrile addition products, many of which have definite boiling-points and are quite stable, are partially dissociated at ordinary temperatures. Thus the addition products with halogens, $RN{=}C\begin{matrix}X\\X\end{matrix}$, are all converted back quantitatively into the alkylisocyanides by treatment with finely divided metals, zinc dust or sodium, which simply abstract the free halogen.

Many of the acylhalide addition products dissociate spontaneously into the components on distillation; these phenomena are perfectly analogous to the dissociation of dry ammonium chloride,

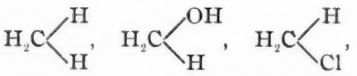
$$H_3N\begin{matrix}H\\Cl\end{matrix} \rightleftharpoons NH_3 + HCl.$$

For this reason the majority of the addition products of the isonitriles can be kept only for a short time; this property rendered futile many attempts to isolate definite addition products. The continual dissociation of such products sets free active or dissociated alkylisocyanide particles, and these slowly condense with one another,

$$XRN{=}C< \rightarrowtail (RN{=}C)_x,$$

giving rise to the so-called alkylisocyanide resins (non-reversible) —products whose molecular weight has not yet been determined and which are perfectly analogous to azulmic or polymerized prussic acid. Consequently, in carrying out an addition reaction with an isonitrile, especially if it requires much time or a temperature above 20°, large quantities of these resinous polymers are formed from which it is possible to isolate the addition product only with great difficulty. Many of the isonitriles themselves, even when perfectly pure, undergo rapid polymerization to resins so that they can be kept only for a very short time. Phenylisocyanide, $C_6H_5N{=}C$, is the most striking instance, as it changes in a few minutes from a colorless to a dark blue liquid and in a few days condenses to a dark brown resin.

Have we not here a possible explanation of the fact that it is impossible to isolate methylene and a large number of its derivatives, although marsh gas, methyl alcohol and chloride of methyl,



each contain a relatively small per cent. of active methylene particles at ordinary temperatures?

The presence of bivalent carbon in the alkylisocyanides having been established, the next question presenting itself was whether prussic acid and its salts contain the cyanogen or the isocyanogen radical. In the latter case, HN : C, MN : C, these substances must be analogous to Gautier's isonitriles. It had hitherto been considered as established, but without sufficient evidence, that prussic acid and the cyanides were cyanogen compounds analogous to the nitriles of Pelouse.

When one considers the physical and physiological properties of prussic acid (boiling-point 25°, sp. gr. 0.7, a violent poison) and contrasts these with the corresponding properties of methylcyanide (boiling-point 81°, sp. gr. 0.81, sweet smelling, harmless oil) and of methylisocyanide (boiling-point 58°, sp. gr. 0.75, a poison) one at once comes to the conclusion that prussic acid, as well as its salts, must belong to the isocyanogen compounds and consequently must contain bivalent carbon.

An exhaustive study of prussic acid and the cyanides establishes this sharply, especially in the case of the salts, from a chemical standpoint. The relation of fulminic acid to prussic acid corroborates the evidence.

You are all familiar with fulminate of mercury—a substance which is made on a commercial scale and used for explosives. It was discovered in 1800 by Howard, and analyzed in 1824 by Liebig in Gay-Lussac's laboratory. We obtain it by dissolving mercury in concentrated nitric acid and adding the resulting solution to ordinary alcohol. It has the empirical formula $HgC_2N_2O_2$, and being obtained from ethyl alcohol, $CH_3—CH_2—OH$, fulminic acid was supposed to have two carbon atoms in its molecule, $H_2C_2N_2O_2$. The constitution of this substance was, for a long time, a great puzzle to chemists. That we have here a substance very closely related to prussic acid was discovered by accident. In working with the mercury salt of isonitromethane it was found that this compound is spontaneously converted at 0° into fulminate of mercury, according to the equation,

$$H_2C{=}NOhg \rightarrowtail \begin{matrix} \| \\ O \end{matrix} \quad \begin{matrix} H \\ HO \end{matrix}\!\!>\!C{=}NOhg \rightarrowtail H_2O + C{=}NOhg.$$

This synthesis led directly to the conclusion that fulminate of mercury possesses a constitution entirely analogous to cyanide of mercury, C=Nhg, *i. e.*, that it contains the isocyanogen radical with bivalent carbon. A further study of the fulminates established this point with precision. Especially striking is the behavior of fulminates towards dilute acids. Liebig and Gay-Lussac stated, in 1824, judging from the odor, that fulminate of silver gives prussic acid with dilute hydrochloric acid. A more careful study of this reaction, in 1894, proved that not a trace of prussic acid, but a substance, formyl chloride oxime, $\begin{matrix} H \\ Cl \end{matrix}\!\!>\!C{=}NOH$, is formed, which possesses the following remarkable properties. Long needles, clear as glass, which decompose and explode with violence at 20°; extremely volatile even at 0° and having an odor similar to prussic acid, which is obviously due to a partial dissociation into fulminic acid. Aqueous silver nitrate converts it quantitatively into chloride and fulminate of silver,

$$\begin{matrix} H \\ Cl \end{matrix}\!\!>\!C{=}NOH + 2AgNO_3 \rightarrowtail AgON : C + AgCl + 2HNO_3.$$

Up to 1897 the presence of bivalent carbon had been established in the following compounds: 1, Carbon monoxide, O:C; 2, the alkyl and aryl isocyanides, R-N:C; 3, prussic acid and the cyanides, NH:C, MN=C; 4, fulminic acid and the fulminates, (HO)N:C, M—O—N=C. 2, 3 and 4 are all compounds containing the isocyanogen radical. In 1897 the presence of bivalent carbon was established in a series of nitrogen-free carbon compounds obtained from acetylene. They are the mono- and dihalogen substituted acetylidenes,

$$\begin{matrix} X \\ H \end{matrix}\!\!>\!C{=}C \text{ and } \begin{matrix} X \\ X \end{matrix}\!\!>\!C{=}C (X{=}Cl, Br \text{ or } I).$$

The corresponding members of the acetylene series, XC≡CH and XC≡CX, do not exist, although we have substances like $CH_3C{\equiv}CI$, $C_6H_5C{\equiv}C{-}X$, whose properties are in marked contrast to those of the acetylidene derivatives.

Diiodacetylidene, which possesses an odor deceptively like that of the isonitriles, dissociates at 100° with violence into iodine and diatomic carbon,

$$I_2C{=}C \rightarrowtail I_2 + C{=}C\ ;$$

the latter can not be isolated as such, but polymerizes explosively to graphite and amorphous carbon. The mono- and dihalogen substituted acetylidenes are all poisonous and spontaneously combustible compounds, possessing, therefore, like methylisocyanide, a marked affinity for oxygen.

Up to the present time it has not been possible to isolate compounds containing bivalent carbon, other than those mentioned above. We are, however, now in a position to explain clearly why we can not hope, by methods now known, to isolate methylene and its homologues as such, although these substances play a great rôle in many of the fundamental reactions of organic chemistry.

In order to approach this point more intelligently let us first consider briefly the properties of unsaturated compounds in general, their possibility of existence, etc.

II. ON THE UNSATURATED COMPOUNDS.

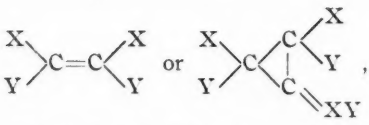
The unsaturated compounds may, first of all, be divided into three categories, namely: I. Those in which two atoms, which may be the same or different, are bound doubly or triply to each other by two or three affinity units, such as olefines; acetylenes; chlorine, $Cl{\equiv}Cl$; oxygen, $O{=}O$; aldehydes, $\begin{matrix} R \\ H \end{matrix}\!\!>\!C:O$; alkylcyanides, $R{-}C{\equiv}N$; nitric acid, $HON\!<\!\begin{matrix} O \\ O \end{matrix}$; sulphur trioxide, $O{=}S\!<\!\begin{matrix} O \\ O \end{matrix}$; etc. II. Those in which an atom itself is unsaturated, *i. e.*, does not exert its maximum valence capacity, as for instance, amines, $R_3{\equiv}N$; thioethers, $R_2{=}S$; methylene derivatives; etc. We must assume that the remaining affinity units are latent, or what is far more probable, especially where two or four affinity units are available, that they mutually polarize each other in a manner entirely similar to unsaturated compounds containing doubly or triply linked atoms.

Finally we have a third class of unsaturated compounds: III. Those containing closed atomic chains, such as trimethylene, $CH_2\langle{}^{CH_2}_{CH_2}$; propylenoxide, $CH_3CH\langle{}^{O}_{CH_2}$; etc., which show apparently a saturated molecular system like the paraffines, and yet react in a manner perfectly analogous to olefines and methylene derivatives.

Fundamentally considered these three classes of unsaturated compounds manifest their chemical activity in the same way; they absorb a great variety of other molecules and thus form combinations, called addition products. How does this union take place? An unsaturated compound with its affinities polarized represents, in reality, a saturated system; it can not, *per se*, show chemical activity. This is also true of molecular systems in which the atoms are bound to one another by single affinity units. The sole basis for reactivity in either case is the presence of a relatively greater or smaller number of dissociated particles. The reactivity of any unsaturated, as well as of a saturated compound, must, in fact, be directly proportional to the ratio of such active particles present. If that ratio is very small, the substance may be entirely inert; if it is greater, absorption of reagents proceeds with regularly increasing speed.

Experience has shown, furthermore, that many unsaturated compounds can not be isolated; but polymerize spontaneously. It is clear that when the per cent. of active particles present in an unsaturated compound becomes relatively great the possibility of their uniting with each other to form condensed molecules increases—in fact, we may imagine a condition in which the active molecules simply can not be prevented from combining with each other. This shows us why we can not isolate and keep substances like formaldehyde, $H_2C{=}O$, or alkylcyanates, $ROC{\equiv}N$, in the monomolecular form. Similarly in many cases where attempts were made to isolate methylene derivatives, like mono- and diphenylmethylene, benzoyl and acetylmethylene,

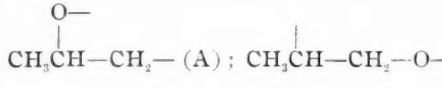
cyanmethylenecarboxylate, $\begin{matrix}CN\\COOR\end{matrix}\rangle C$, a spontaneous polymerization to the di- or trimolecular systems,



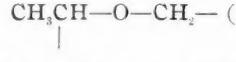
took place. One further point with reference to unsaturated compounds must now be presented.

Intramolecular Rearrangement Shown by Unsaturated Systems.

From the discussion presented above it is obvious that trimethylene and propylenoxide, belonging to class III, must contain a small percentage of active particles; the dissociation of the triatomic ring in the former case can lead to only one form of active molecule, namely, $—CH_2—CH_2—CH_2—$; whereas propylenoxide may give the following three active molecules:



and



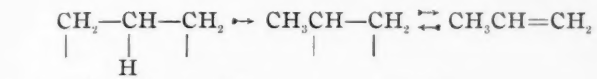
Since propylenoxide absorbs dry ammonia or hydrogen chloride, as was proved by especially careful and exhaustive experiments, giving addition products of the general formula

$$CH_3CHOH—CH_2X \ (X=Cl \text{ or } NH_2),$$

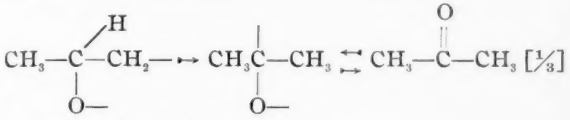
the only possible conclusion that can be reached is that propylenoxide contains relatively more active (A) than active (B) or (C) molecules; consequently the absorption reactions proceed by preference in *only one* of three theoretically possible directions.

When trimethylene or propylenoxide is heated or placed in contact with various catalytic agents, the per cent. of active particles must naturally increase and when a definite limit has been reached a spontaneous transformation of trimethylene into propylene and of propylenoxide into propionicaldehyde ($^2/_3$) and acetone ($^1/_3$) takes place; both reactions are non-reversible.

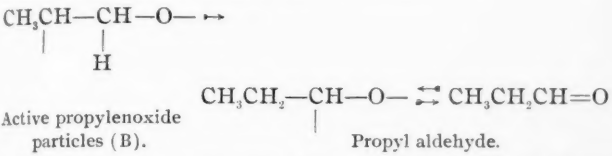
These results can only be explained in the following manner: aside from the increase in active particles, dissociation in other parts of the molecule and especially of hydrogen from carbon must also take place. Consequently the following intramolecular addition reactions finally occur spontaneously:



Active trimethylene particles. Propylene.



Active propylenoxide, particles (A). Acetone.

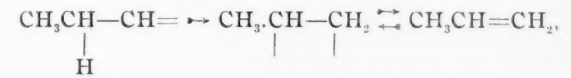


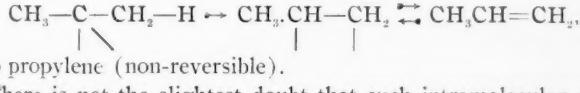
Active propylenoxide particles (B). Propyl aldehyde.

It is interesting to note that the active (B) propylenoxide molecules which are present in smaller ratio suffer rearrangement more readily than the active (A) molecules. The active (C) molecules, on the other hand, must be present in far smaller amount and certainly no transformation of propylenoxide to vinylmethyloxide, $CH_2=CH—OCH_3$, takes place.

It is important to realize that propylenoxide, acetone and propionaldehyde are isomers, but do not stand in a tautomeric relation to one another. This is also true of trimethylene and propylene, as well as of α- and β-amylene and isoamylene, etc.

Similarly it can be rigidly shown by experiment that α- and β-propylidene, $CH_3CH_2CH=$ and $(CH_3)_2C=$, which are spontaneously combustible substances not capable of isolation as such, transform themselves by intramolecular addition,





into propylene (non-reversible).

There is not the slightest doubt that such intramolecular addition reactions are the basis of the majority of our synthetic methods for making cyclic compounds. The cycloparaffines in Russian petroleum are probably formed from ordinary paraffines

by dissociation into hydrogen and methylene derivatives and the latter then spontaneously transform themselves, by intramolecular addition, into penta- and hexamethylene rings.

On the Reactions of Paraffines and Benzene Derivatives.

The reactions of paraffines and benzene derivatives towards halogens, nitric and sulphuric acids, whereby substitution products are formed are still interpreted in the text-books from the standpoint of metalepsis or substitution, although a vast amount of evidence has accumulated which makes this axiomatic assumption improbable.

The fact that ethane and benzene, for instance, decompose into hydrogen and into ethylene and diphenyl at 800° and 600°, respectively, proves that an extremely small per cent. of these molecules must exist at ordinary temperatures in an active or dissociated condition,

$$CH_3CH_3 \rightleftarrows CH_3CH_2- + H- ;$$

and $CH_3CH_3 \rightleftarrows C_2H_4 + 2H-$ or $C_6H_6 \rightleftarrows C_6H_5- + H-$.

The same is true of ammonia,

$$H_3N \rightleftarrows -NH_2 + H- \text{ and } 2H- + =NH \text{ and } \equiv N + 3H-,$$

and of a great variety of other non-ionizable hydrogen compounds. Consequently, when chlorine or nitric acid reacts with benzene or ethane to give the monochlor or mononitro substitution products we have these reagents, in the *active molecular* condition, simply uniting by addition with the dissociated ethane or benzene particles,

$$\begin{array}{l} \text{Cl=Cl} + \text{H—C}_2\text{H}_5 \rightarrowtail \begin{array}{l}\text{Cl=Cl}\\ \text{H}\quad\ \text{C}_2\text{H}_5\end{array} \\ \text{or} \\ \begin{array}{l}\text{O}\\ \|\\ \text{HO—N—O}\\ |\quad|\end{array} + \text{H—C}_6\text{H}_5 \rightarrowtail \begin{array}{l}\text{O}\\ \|\\ \text{HO—N—OH}\\ |\\ \text{C}_6\text{H}_5\end{array} ; \end{array}$$

the resulting addition products then lose hydrogen chloride and water respectively, and thus give the monochlor or nitro substitution product of the mother substance. From this point of view all so-called substitution reactions belong to the category of addition reactions.

What is now especially needed in order to place the reactions

of organic chemistry on an exact mathematical basis is a precise method of determining the ratio of active particles present at various temperatures in the case of the unsaturated, as well as the saturated, compounds.

As the substances under discussion are almost exclusively non-electrolytes, the sole methods that suggest themselves for this purpose are determinations of the speed of decomposition, as well as of addition reactions.

The above discussion makes it evident that all unsaturated compounds belonging to classes I and III contain a small and relatively varying per cent. of active particles with one or more carbon atoms temporarily in an active or *trivalent* condition; the same is true of compounds containing hydrogen bound to carbon—paraffines, C_nH_{2n+1}—H, benzene derivatives, etc. The isolation of compounds containing trivalent carbon as such, I believe, however, to be an impossibility. Gomberg's triphenylmethyl, for instance, has recently been proved by him to be a bimolecular aggregate, $C_{38}H_{30}$—not identical with hexaphenylethane—which, however, like the above-mentioned compounds, contains a very small percentage of active triphenylmethyl, $(C_6H_5)_3{\equiv}C$—, particles in dynamic equilibrium with the bimolecular aggregate; as soon as the percentage of triphenylmethyl particles is increased by heat or by means of catalytic agents a spontaneous polymerization to the real hexaphenylethane (non-reversible) takes place.

We are now in a position to consider the evidence showing that methylene and its homologues play a great rôle in many of the fundamental reactions of organic chemistry which have hitherto been explained on the basis of substitution.

III. ON THE REACTIONS OF THE MONATOMIC ALCOHOLS AND THE ALKYLHALOIDS.

The experiments which first suggest themselves as a means of isolating methylene and its homologues are: 1, Dissociation of olefines as ethylene,

$$CH_2{=}CH_2 \rightleftarrows 2CH_2, \ \beta\text{-butylene},$$

$$CH_3CH{=}CH{-}CH_3 \rightleftarrows 2CH_3CH{=}, \text{ etc.}$$

Since ethylene gives hydrogen and acetylene by heat and the higher olefines also decompose with evolution of hydrogen, there

was little prospect of success by experiments in this direction. 2, Dehydration of the mon-atomic alcohols, $C_nH_{2n+1}OH$, or removal of halogen hydride from the alkylhalides, $C_nH_{2n+1}X$; naturally only primary and secondary derivatives, RCH_2X and $\begin{matrix} R \\ R' \end{matrix}\!\!>\!CHX$ (X=OH, Cl, Br or I), and not tertiary compounds, $R_3{\equiv}C{-}X$, can yield methylene and its homologues. Furthermore, since many of the alcohols and alkylhalides containing more than one carbon atom in the molecule are known to give olefines by dissociation, dehydration, or treatment with alcoholic potash respectively, the conclusion might naturally at first be drawn that only a direct olefine dissociation existed in these cases. From a purely theoretical standpoint, however, it is clear that a primary or secondary alkylhalide or a corresponding alcohol with more than one carbon atom in the molecule may dissociate with loss of halogen hydride or water in two possible ways: It may undergo (1) methylene dissociation, as

$$R.CH_2.CH\begin{matrix} X \\ H \end{matrix} \rightleftharpoons RCH_2CH= + HX, \text{ and } (RR')C\begin{matrix} H \\ X \end{matrix} \rightleftharpoons (RR')C= + HX;$$

or (2) olefine dissociation, as

$$RCH_2{-}CH_2X \rightleftharpoons \begin{matrix} RCH{-}CH_2 \\ | \quad | \\ CH_3{-}CH{-}CH{-}CH_3 \end{matrix} + HX \text{ and } \begin{matrix} CH_3CH_2 \\ CH_3 \end{matrix}\!\!>\!CHX \rightleftharpoons \begin{matrix} \quad | \quad | \\ CH_3CH_2CH{-}CH_2 \end{matrix} + HX;$$

or both kinds of dissociation may take place simultaneously.

A third kind of dissociation where the hydrogen atom does not come from the atom containing the X or from a carbon atom adjacent to it is also possible and at times important, but it need not be considered in this connection.

An exhaustive study of the primary and secondary alcohols and alkylhalides, covering a period of nine years, has proved very conclusively that these substances undergo methylene dissociation only.

Preliminary experiments with alcohols and alkylhalides where no olefine dissociation is possible, *i. e.*, in the methane,

$CH_2\langle^{H}_{X}$, toluene, $C_6H_5CH\langle^{H}_{X}$, diphenylmethane, $(C_6H_5)_2C\langle^{H}_{X}$,

acetone and acetophenone, $CH_3COCH\langle^{H}_{X}$, and $C_6H_5COCH\langle^{H}_{X}$,

malonic and cyanacetic ester series,

$$(COOR)_2C\langle^{H}_{X} \quad \text{and} \quad \begin{matrix} CN \\ COOR \end{matrix}\rangle C\langle^{H}_{X},$$

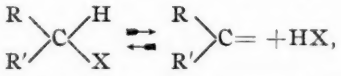
have proved that all these compounds have very low dissociation points—never above 300° in the aromatic nor, with few exceptions, in the aliphatic series. Nevertheless it was found impossible to isolate the methylene derivative as such in any case; there was either a spontaneous conversion to a di- or trimolecular polymer, an olefine or a trimethylene derivative, or a conversion to resinous polymers analogous to azulmic acid and the alkylisocyanide resins. Most important was the discovery that these nascent or active methylene residues, $\begin{matrix} Z \\ Y \end{matrix}\rangle C=$, are always spontaneously combustible, burning often with marvelous evolution of heat to the corresponding oxides, $\begin{matrix} Z \\ Y \end{matrix}\rangle C=O$; this was not surprising in view of the properties of the methylene derivatives described above. Furthermore, the affinity of unsaturated carbon for oxygen is strikingly shown by the fact that these residues have the power of decomposing water,

$$\begin{matrix} Z \\ Y \end{matrix}\rangle C= + O=H_2 \rightarrow \begin{matrix} Z \\ Y \end{matrix}\rangle C=O + 2H—,$$

with evolution of hydrogen.

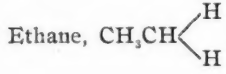
A subsequent investigation of the primary and secondary alcohols and alkylhalides containing more than one carbon atom proved, first of all, that all these substances have comparatively low points of dissociation. In no case was the decomposition point found to be higher than 700°; it was often as low as 160° to 300°. The products of dissociation are water or halogen hydride and C_nH_{2n} respectively; and the latter, as emphasized

above, is invariably methylene or a homologue and never an olefine. This naturally means that all these compounds are partially dissociated in this way at ordinary temperatures,

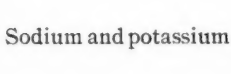


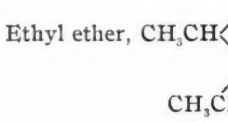
relatively more the lower the actual decomposition point.

It is, therefore, possible that in all the interactions of the primary and secondary alkylhalides with other substances, such as salts, ammonia, metals, benzene, etc., they do not act as such, but by virtue of being partially dissociated. An enormous amount of evidence has accumulated in favor of this conclusion. Let us consider chiefly the results obtained in the ethyl series, including ethyl alcohol and its derivatives. The dissociation or decomposition point of the following compounds containing ethyl has been determined with a fair degree of accuracy:

Ethane,  , 800°

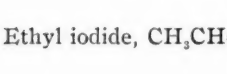
Ethyl alcohol, , 650°

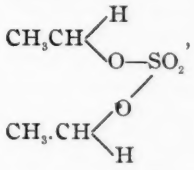
Sodium and potassium ethylate,  , 250°

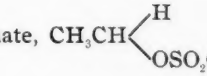
Ethyl ether,  , 550°

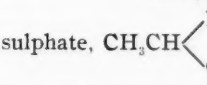
Ethyl chloride, , 600°

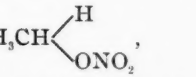
Ethyl bromide, , 500°

Ethyl iodide,  , 400° (?)

Diethyl sulphate,  , 200°

Monoethyl sulphate,  , 160°

Ethyl potassium sulphate,  , 250°

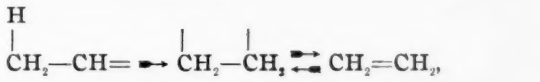
Ethyl nitrate,  , 200° (?)

Ethane, ethyl chloride and bromide, when heated to the temperatures named, give ethylene and hydrogen or halogen hydride respectively, and on cooling these products do not again recombine. We can, therefore, obtain ethylene quantitatively from chloride or bromide of ethyl by simply passing their vapors through tubes heated to the decomposition point. Nevertheless it is impossible to obtain more than very small amounts of ethylene from the ethylhalides by means of alcoholic potash, caustic potash or quicklime; in these cases ethyl ether or ethyl alcohol is the chief reaction product even when the ethyl halide is passed over quicklime in tubes heated to from 300° to 500°.

Furthermore, the per cent. of ethylene obtained varies remarkably with the temperature, the concentration and with the nature of the halogen in the alkylhalide used.

The conclusions finally reached from these data and also from an exhaustive study of the behavior of the various alkylhalides, nitrates, sulphates, alkylpotassium sulphates towards heat, sodium ethylate, caustic potash, quicklime and other salts are that ethylene can not possibly be a primary product of dissociation of the ethylhalides, sulphates and nitrates, and of free ethyl alcohol.

The ethylene, when obtained, is formed from ethylidene by an intramolecular addition reaction,



which is not reversible. A similar intramolecular change always, in fact, takes place whenever an olefine is formed, whether from a primary or secondary alcohol, or from a corresponding alkyl halide sulphate or nitrate. This transformation is perfectly analogous to the conversion, discussed above, of trimethylene and of propylenoxide into propylene, propionaldehyde and acetone.

When ethyl alcohol or ethyl ether is heated to its dissociation point the ethylidene interacts at once in great part with the other dissociation product, water, to give hydrogen and acetaldehyde,

$$CH_3CH= + O=H_2 \rightarrowtail CH_3CH : O + 2H—.$$

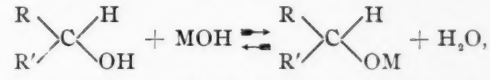
In the case of ether, since there are two ethylidene molecules to one of water, the atomic hydrogen is, in part, absorbed by ethylidene to give ethane. Finally, a portion of ethylidene, 20 and 37 per cent. respectively, is transformed, by intramolecular addition, into ethylene. The most striking proof that ether is dissociated into water and $2C_2H_4$ particles is the following: On passing ether vapor over phosphorus pentoxide at temperatures varying from 200° to 400° ethylene is formed quantitatively.

The primary and secondary alcohols and their corresponding ethers being in a state of very slight dissociation at ordinary temperatures we are able to understand perfectly their behavior towards oxidizing agents. The alkylidenes are all spontaneously combustible substances possessing a great affinity for oxygen. Absolutely pure dry ethyl ether, dissociation point 550°, contains a sufficient per cent. of ethylidene particles at ordinary temperatures to burn very slowly in dry oxygen; sodium ethylate, dissociation point 250 , on the other hand, being dissociated to a far greater extent, burns with great violence in dry air. Ethyl alcohol, dissociation point 650°, is not capable of burning in the air; if, however, we increase the per cent. of ethylidene particles by means of catalytic agents, enzymes, platinum sponge, etc., it, too, oxidizes readily, with incandescence with platinum sponge, giving acetic acid.

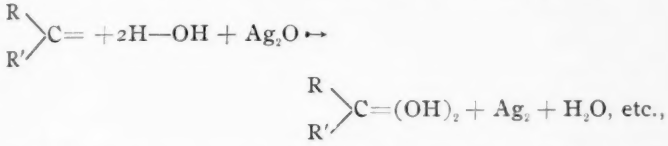
The aldehydes, R—CH : O, as has long been known, reduce Fehling's solution and silver solutions with great ease. This is due to the presence of oxyalkylidene particles, $\begin{matrix} R \\ \diagdown \\ HO \diagup \end{matrix}\!\!>C=$, which

burn at the expense of the oxygen in the water.

The discovery that all primary and secondary alcohols reduce silver oxide to metallic silver in aqueous solution in the presence of caustic alkalies has only very recently been made. The function of the alkali is obviously to form first the metallic alcoholate,

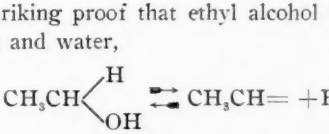


which, having a far lower dissociation point than the free alcohol, causes a great increase in the per cent. of alkylidene particles present: consequently, the following reaction can take place:

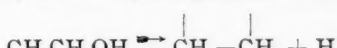


giving, as the end result, a fatty acid in the case of primary alcohols.

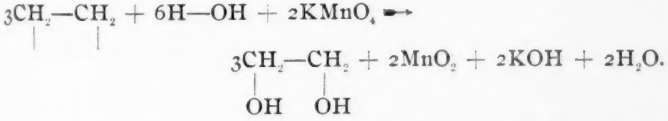
The most striking proof that ethyl alcohol is dissociated only into ethylidene and water,



i. e., contains no ethylene particles, is the following: Ethyl alcohol, containing 1 molecule of aqueous sodium hydroxide, gives, in the cold, with potassium permanganate solution, practically acetic acid only. If any active ethylene particles were present,



these must necessarily, in view of the work of Wagner with olefines and permanganate, be first converted by oxidation to ethylene glycol,



Analogous results would naturally be expected in the case of all the homologous primary and secondary alcohols. Now a

primary alcohol invariably first gives, by oxidation with potassium permanganate or other oxidizing agents, the corresponding fatty acid. Glycols or their oxidation products have never been observed in such cases.

The fact that ethyl alcohol gives glyoxal, glyoxylic and oxalic acids with nitric acid is no exception to this rule, because these substances result from the hydrolysis and oxidation of isonitrosoacetaldehyde, which is formed by the action of nitrous acid on acetaldehyde as follows:

$$H{-}CH_2CHO + O{-}NOH \rightarrow HO{-}\underset{\displaystyle CH_2.CH:O}{\overset{\displaystyle HON}{\overset{\|}{N}}}{-}OH \rightarrow \underset{\displaystyle CH{-}CH:O}{\overset{\displaystyle HON}{\overset{\|}{N}}} + H_2O.$$

The behavior of aldehydes and of primary alcohols towards aqueous or solid caustic potash also leads to the conclusion that only alkylidene dissociation occurs. Ethyl alcohol gives, at 250°, with an excess of caustic potash, hydrogen and potassium acetate quantitatively,

$$CH_3CH\begin{matrix}H\\OK\end{matrix} + 2KO{-}H \rightarrow CH_3CH{=} + 3KO{-}H \rightarrow$$

$$CH_3CH(OK)_2 + 2H + KOH \rightarrow \begin{matrix}CH_3\\KO\end{matrix}\!\!>\!C{=} + 2H{-}OK + H_2 \rightarrow$$

$$\begin{matrix}CH_3\\KO\end{matrix}\!\!>\!C(OK)_2 + 2H + H_2 \rightarrow CH_3C(OK)_3 + 2H_2.$$

If any of the potassium ethylate, which is first formed, were dissociated into ethylene and caustic potash,

$$CH_3CH_2OK \rightleftarrows \underset{|}{CH_2}{-}\underset{|}{CH_2} + HOK,$$

the olefine must naturally give, besides hydrogen, ethyleneglycol,

$$\underset{|}{CH_2}{-}\underset{|}{CH_2} + 2H{-}OK \rightarrow \underset{OK}{\overset{|}{CH_2}}{-}\underset{OK}{\overset{|}{CH_2}} + H_2,$$

or its decomposition products; these are, however, not formed. The reaction with potash-lime and primary alcohols is so deli-

cate and accurate that it has been suggested by Hell as a means of determining the molecular weight of an unknown primary alcohol.

As mentioned above, ethyl ether is the chief product when ethyl halides are treated with alcoholic potash, or with dry sodium ethylate; this is also true when dry silver oxide and ethylhalides are used.

These reactions, which have been interpreted by Williamson and others on the basis of double decomposition or of minute ionization, must obviously be attributed to the absorption by the ethylidene of alcohol or of water, which is set free by the action of the halogen hydride particles on the sodium ethylate or silver oxide respectively,

$$CH_3CH= + H—OC_2H_5 \rightarrow CH_3CH_2OC_2H_5,$$

or

$$2CH_3CH= + H_2=O \rightarrow CH_3CH\begin{matrix}H\\O\\CH_3CH\end{matrix}\!\!\begin{matrix}\\\\H\end{matrix}.$$

We are now able to consider an entirely new explanation of the function of sulphuric acid, or of phenyl sulphonic acid, in converting ethyl alcohol into ether. Sulphuric acid acts, first of all, with alcohol at ordinary temperatures to give both mono- and diethyl sulphate; the first stage in the reaction can not be ascribed to the union of ethylidene, formed by dissociation of alcohol, with free sulphuric acid since ethyl ether, which is relatively more dissociated than alcohol, acts *only very* slowly with concentrated sulphuric acid at ordinary temperatures to give monoethyl sulphate. Furthermore, since sulphuric acid itself is completely dissociated into its components, sulphur trioxide and water, at 400°, it is extremely probable that monoethyl sulphate is formed by the union of sulphur trioxide, present by dissociation,

$$H_2SO_4 \rightleftarrows SO_3 + H_2O, \text{ with alcohol,}$$

$$O_2S\begin{matrix}—O\\|\\|\end{matrix} + H—OC_2H_5 \rightarrow O_2S\begin{matrix}OH\\OC_2H_5\end{matrix}.$$

Now it is well known that ether formation in a mixture of sulphuric acid and alcohol begins perceptibly only at 95° and

proceeds *very* slowly at that temperature. The favorable temperature for ether manufacture is 140°. This is self-evident in view of the following considerations: Primary and secondary ethyl sulphate possess the dissociation points 160° and 200° respectively; consequently, these substances must be dissociated at 140° to a very great extent into sulphuric acid and one or two molecules of ethylidene respectively. Addition of alcohol at 140°, therefore, simply necessitates a combination with the ethylidene particles,

$$CH_3CH= + H—OC_2H_5 \rightarrowtail CH_3CH_2OC_2H_5,$$

to give ether, and this process can naturally go on indefinitely.

When ethyl alcohol is mixed with an excess of concentrated sulphuric acid and heated to 160°, no ether, but some ethylene, is formed; in fact, this method is still suggested and used as the best means of preparing ethylene.

The yield of olefine, however, can never be raised above 20 per cent. of the theory and the operation is extremely tedious because carbonization and formation of sulphur dioxide takes place to a very marked extent. These results are now easily understood. The ethylidene molecules, formed by dissociation of ethylated sulphuric acid, burn chiefly at the expense of the oxygen present in sulphuric acid,

$$CH_3CH= + O=SO_2 \rightarrowtail CH_3CH : O + SO_2,$$

and the resulting acetaldehyde is then at once charred by the vitriol present. Only 20 per cent., at the utmost, of the ethylidene particles escape this oxidation by intramolecular conversion to ethylene.

Finally we may summarize the conclusions reached in the above discussion as follows:

The valence of carbon is not a constant. At definite temperatures, which vary remarkably with the nature of the groups bound to it, a carbon atom becomes spontaneously dyad. Below these limits there is dynamic equilibrium between bivalent and quadrivalent carbon. The existence of carbon compounds containing bivalent carbon has been definitely established; methylene chemistry plays a great rôle in many of the fundamental reactions of organic chemistry.

The conception of substitution or metalepsis, which has been

our guide in interpreting the reactions of carbon chemistry since 1833, is no longer tenable. It must be replaced by the conception of dissociation in its broadest sense. Fundamentally speaking, there are but two classes of carbon compounds—the saturated and the unsaturated. Excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an addition product. The one molecule being unsaturated and partially in an active molecular condition absorbs the second molecule because it is partially split or dissociated into two active portions. The resulting addition product then often dissociates spontaneously, giving two new molecules. The similarity of such reactions to those called ionic is at once apparent, but their relationship can not, in the present state of our knowledge, be clearly understood.

A REVISION OF THE ATOMIC WEIGHT OF IODINE.

By Gregory Paul Baxter.

Received September 28, 1904.

The atomic weight of iodine has been for some time considered one of the best determined of chemical constants, owing to the extremely concordant results of Stas and Marignac, who both deduced the value 126.85 (O = 16.000) from syntheses of silver iodide. Within the last two years, however, two series of determinations, one by Ladenburg and one by Scott, have yielded results over one-tenth of a unit higher than the above. Ladenburg's method consisted in heating silver iodide in a current of chlorine until all the iodine had been displaced, and gave the result 126.96, while Scott, like Stas and Marignac, synthesized silver iodide and obtained in two analyses the values 126.96 and 126.98.[1] The anomaly in the atomic weights of iodine and tellurium has always been of the greatest interest, and has led to a large number of investigations upon the atomic weight of tellurium during the last few years, which have shown conclusively that this value lies in the neighborhood of 127.6. The doubt thrown upon the

[1] Very recently, since the work described in this paper was completed, Köthner and Aeuer have published a preliminary notice of experiments involving syntheses of silver iodide as well as a repetition of Ladenburg's work, from which they conclude that the atomic weight of iodine cannot be lower than 126,963. Details of their work are not given. See *Ber. d. chem. Ges.*, **37**, 2536.

atomic weight of iodine by the work of Ladenburg and Scott makes it imperative to subject iodine to further careful investigation.

PART I.

THE RATIO OF SILVER TO SILVER IODIDE.

In choosing a compound for an atomic weight determination, two of the most important points to be considered are the stability of the substance under various conditions, and the certainty with which the atomic weights are known of those elements, besides the one under examination, which compose it. In the case of iodine, few of its compounds are stable, and the only one which satisfies both the above conditions is silver iodide. Accordingly, synthesis of silver iodide from a weighed amount of silver was selected for the first method of investigation.

Purification of Materials.—The problem of purification of materials was a comparatively simple one. Silver was prepared as follows: To a solution of silver nitrate which had been made strongly acid with nitric acid, there was added a large excess of concentrated hydrochloric acid. After the precipitate had been washed many times wth pure water, it was reduced to metallic silver by means of a solution of sodium hydroxide and invert sugar. The silver was washed well with water and fused with a blowpipe on charcoal. Surface impurities were removed by scrubbing the buttons with sand, and boiling them, first with dilute hydrochloric acid, and then with ammonia. Next, the whole of the process, just described, was repeated, but with reagents which had been purified with the greatest care. Water and acids were freshly distilled, the sodium hydroxide was electrolyzed in a platinum dish until free from iron, and the final fusion was carried out in a porcelain crucible lined with the purest lime. This lining was made by the ignition of a mixture of reprecipitated calcium carbonate and recrystallized calcium nitrate. After the buttons had been cleansed as before, the silver was deposited electrolytically by making one button the cathode, the other buttons in succession the anode, in a cell containing a strong solution of silver nitrate made by dissolving one of the buttons in pure nitric acid. Connection was made with the battery by means of a platinum wire, which, however, did not dip into the solution. The crystals

of silver were washed, first with water, then with ammonia, and again several times with water. Finally they were dried and fused in a current of hydrogen on a boat of pure lime contained in a porcelain tube. The hydrogen was generated electrolytically from a cell composed of zinc amalgam, hydrochloric acid, and platinum, and was purified from hydrochloric acid and dried by passing over beads moistened with caustic potash solution and then over solid potassium hydroxide. The silver was cut into fragments weighing from 3 to 5 grams each by means of a clean chisel and anvil, and the iron adhering to the surface was removed by warming the pieces repeatedly with fresh portions of dilute nitric acid, until iron could no longer be detected in the acid. The fragments were washed thoroughly with the purest water, then with ammonia, and again with water as before. They were allowed to dry in the air, and finally the last traces of moisture were eliminated by heating in a vacuum, since silver which is heated to a high temperature in the air has been shown by Stas to absorb considerable oxygen.[1] Silver prepared in a similar fashion by investigators in this laboratory has always been found to be pure,[2] and since two different samples were used in the following work with identical results, there can be no doubt of the purity of that employed here. Furthermore, one synthesis of silver chloride, carried out with a portion of this silver by Wells in the investigation of Richards and Wells upon the atomic weight of chlorine, yielded the value 35.467, which is identical with the average of other similar determinations made with his own silver.

The chief impurities in commercial iodine are halogens of lower atomic weight and iodide of cyanogen. These were removed by dissolving iodine in a strong solution of half its weight of potassium iodide, and distilling the greater portion of the iodine from a retort into a flask cooled with cold water. The iodine thus obtained was next converted into hydriodic acid by covering it with considerable water and passing through the solution a stream of hydrogen sulphide. This gas was generated by the action of dilute sulphuric acid upon ferrous sulphide, and was purified by bubbling through three gas washing-bottles containing water and through two towers filled with beads moistened with water. The reaction between the hydrogen sulphide and the iodine results

[1] *Œuvres Complètes*, **3**, 125.

[2] *Proc. Am. Acad.*, **28**, 22; **29**, 46; **31**, 173; **39**, 249.

chiefly in the formation of hydriodic acid and the precipitation of sulphur, although a small quantity of sulphuric acid is always produced. Iodide of cyanogen with hydrogen sulphide yields hydrocyanic acid, hydriodic acid, and sulphur.[1] The solution was first boiled for a short time until the sulphur had clotted together, and the sulphur was removed by filtration. The clear solution was then boiled for several hours in order to eliminate the hydrocyanic acid.[2] Finally the hydriodic acid was partially converted into iodine by distilling the solution with potassium permanganate. This permanganate must also have had the effect of oxidizing any organic impurities. Since in the reaction three-eighths of the iodine remains in the form of iodides, the resulting iodine was thus subjected to a second distillation from an iodide. The product was again converted into hydriodic acid by means of hydrogen sulphide, and this again into iodine by recrystallized potassium permanganate which was free from even a trace of chlorine. Since in the case of bromine it has already been shown that two distillations from a pure bromide are sufficient to free this element from chlorine,[3] three distillations of iodine from a solution of an iodide should insure complete elimination of chlorine and bromine, even if the original substance were very impure. The purified iodine was again converted into hydriodic acid by hydrogen sulphide, and this into ammonium iodide by an excess of freshly distilled ammonia. This material was used in the analyses made with Sample I.

It was suggested by Professor T. W. Richards that an undiscovered element resembling the halogens, but of a higher atomic weight, might exist, and an attempt to detect the existence of such an element was carried out as follows: One pound of iodine was purified as described above, but the process of converting the iodine into hydriodic acid by hydrogen sulphide, and the hydriodic acid into iodine by potassium permanganate, was repeated four times. The iodine obtained in the last distillation with permanganate, amounting in all to about 50 grams, was set free in four fractions by introducing the permanganate in portions of about 2 grams each. An element belonging to the halogen family, and of higher atomic weight than iodine, should be more easily

[1] Dammer: *Handb. d. anorg. Chem.*, II, **1**, 432.
[2] Richards and Singer: *Am. Chem. J.*, **27**, 205.
[3] *Proc. Am. Acad.*, **28**, 17; **31**, 165; **37**, 106; **39**, 249.

set free than iodine, hence the first of the four fractions should have contained nearly all of such an element which occurred in the pound of iodine. Each one of the fractions was once distilled with pure water, and was then converted into ammonium iodide, as in the case of Sample I. The first fraction was Fraction 1 of Sample II, the fourth was Fraction 4 of Sample II. No difference in appearance between these samples and Sample I or even the original crude iodine could be detected.

All reagents used in the course of the purification or in the analyses were carefully purified. Acids and ammonia were redistilled, usually with the use of a platinum condenser. The water was distilled twice, once from alkaline permanganate, once from a solution containing a trace of sulphuric acid. In both distillations block-tin condensers were used.

Method of Analysis.—In order to convert a known weight of silver into silver iodide the following method was employed. The silver was dissolved in nitric acid in an Erlenmeyer flask, into the neck of which a column of glass bulbs was ground.[1] The acid consisted of the constant boiling distillate diluted with an equal volume of water. Solution was effected by warming so gently that almost no gas was evolved. When the silver was completely dissolved, the solution was diluted with an equal volume of water and was heated until all nitrous acid was destroyed and all oxides of nitrogen were expelled. It was then transferred to one of the precipitating flasks. These were Erlenmeyer flasks of 1 and 2 liters capacity, into the necks of which glass stoppers had been carefully ground.[2] Into the solution of silver nitrate, which had been diluted until not more than 1 gram of silver was contained in 100 cc., and to which an excess of ammonia had been added, a slight excess of the solution of pure ammonium iodide, which also had been diluted until it was not stronger than 1 per cent., was poured. The flask was stoppered and shaken for some time and allowed to stand for about a day. Then a very slight excess of nitric acid was introduced, the flask again shaken for some time, and allowed to stand for one or two days until the solution above the precipitate seemed perfectly clear. The precipitate was washed by decantation with 1 per cent. nitric acid at least eight times, and transferred with water to a

[1] Richards: *Proc. Am. Acad.*, **25**, 198.
[2] Richards: *Ibid.*, **28**, 24.

weighed Gooch crucible through which the washings had been poured. Finally the crucible was heated in an electric air-bath for several hours, first at 100° to 110°, then at 200° C.

Although silver iodide is very slightly sensitive to diffused daylight, the operations of precipitation and filtration were performed in a large cupboard lighted wth orange light. When taken out of the dark room, the flask was enveloped in several thicknesses of black cloth.

The tendency of precipitated silver iodide to pass into a milky condition when washed with pure water is very marked. It has been found by Stas and others that if the water is previously heated to about 60° C., and plenty of time is allowed for the precipitate to settle at that temperature, this tendency can be overcome. When washed with warm water, however, silver iodide adheres to the flask to such an extent that it is impossible entirely to remove the precipitate, even by vigorous rubbing. The conditions which were found most favorable for preserving the precipitate in such a state that it could be easily and rapidly manipulated were as follows: In the first place precipitation was carried out in ammoniacal solution, because the silver iodide clotted together much more rapidly than in acid solution, owing probably to the greater solubility of silver iodide in the alkaline solution. A large excess of nitric acid also coagulated the precipitate, but since the acid caused the separation of a large amount of iodine, it could not be employed in the present case. Dilute nitric acid, on the other hand, proved to be a satisfactory medium for washing the silver iodide, for it was found that the precipitate could be washed indefinitely with even 1 per cent. nitric acid wihout passing into the colloidal state. The washings obtained in this way, when treated with an iodide, gave no trace of opalescence even on long standing, showing that silver iodide is insoluble in the dilute acid. When silver iodide which has been washed with nitric acid only is dried at a high temperature, a loss of iodine takes place, owing to action on the silver iodide by the nitric acid. This was evident from the dark color of the iodide. In order to avoid this difficulty, the precipitate was finally transferred to the Gooch crucible with pure water, sometimes after one rinsing with water. The nitric acid was so completely displaced by this means that the precipitate did not darken even on fusion. Unfortunately, even this slight

washing with water in most cases caused some of the precipitate to pass through the crucible in a colloidal condition; consequently, these last washings were collected separately. In the earlier analyses the silver iodide in this colloidal solution was determined by first boiling the solution with a small quantity of ammonium iodide until the silver iodide was coagulated, and then collecting the precipitate upon a small filter-paper, together with the asbestos shreds and any silver iodide which were contained in the remainder of the filtrate and washings. As a rule, this operation was performed only after the wash waters had stood for two or three days, in order that insoluble matter might have time to settle. The bottom of each flask was rubbed gently with a rubber-tipped stirring rod to detach adhering particles. Finally the filter-paper was burned in a weighed porcelain crucible at as low a temperature as possible, for if a high temperature is employed, a loss of silver iodide by volatilization occurs. The ash was treated with a drop of nitric acid, and, after warming, a drop of ammonium iodide solution was added. The excess of acid and ammonium salt was driven off and the crucible was weighed.

In these earlier analyses it was found necessary to detach small particles of adhering silver iodide from the neck of the precipitating flask by rubbing with a rubber-tipped rod. Later a better method was devised for collecting this small amount of precipitate, together with that contained in the colloidal washings. First the flask was rinsed with a small quantity of a solution of potassium cyanide, and this solution was poured into the colloidal washings. Then the solution was evaporated to small bulk and electrolyzed in a weighed platinum crucible, which was heated to 130° in an electric oven, and was finally reweighed. The film was dissolved in dilute nitric acid and the solution precipitated with an excess of ammonium iodide. This precipitate of silver iodide, if over 0.0005 gram in weight, was collected on a small weighed Gooch crucible, and the filtrate, together with the original filtrate and wash waters, was passed through a small filter repeatedly until clear. If the precipitate weighed less than the above quantity, it was collected wholly upon a filter. These filters were, of course, ignited and treated as before. The weight of the silver iodide and asbestos was used in computing the results, the weight

of electrolyzed silver serving merely as a check upon the weight of silver iodide.

In order to drive off the last traces of moisture from the silver iodide it was fused in a porcelain crucible. The bulk of the precipitate, freed as completely as possible from asbestos, was transferred to a clean crucible, which was then weighed with its cover. The crucible and cover were placed inside a large porcelain crucible, and were heated until fusion took place. A temperature much above the melting-point of silver iodide was avoided, since this substance is distinctly volatile at higher temperatures. The loss in weight was then determined. The fused salt, when cold, was light yellow in color, with no trace of darkening, showing that no appreciable loss of iodine had taken place.

The density of pure silver iodide was found by displacement of water. Three determinations were made with material which had been fused in a porcelain crucible and cooled by pouring the fused mass upon a cold tile. The solidified salt was broken into small fragments and was introduced into a weighed pycnometer for solids, which was then reweighed. Water sufficient to cover the salt was introduced into the pycnometer and the system was placed in a vacuum desiccator which was kept exhausted until it seemed probable that all air had been extracted from the solid. Then the pycnometer was immersed in a bath at 25° C. and exactly filled with water. Finally the system was weighed. Two more determinations were carried out with material which had been cast into sticks by pouring the fused salt into a porcelain boat. These sticks were used in an elongated form of pycnometer for solids.[1] The average of the last two experiments is undoubtedly more accurate than that of the first three, since it was extremely difficult to pump out the air from the more porous material used in the first experiments.

The vacuum correction for silver iodide, when weighed with brass weights, calculated from this value for its specific gravity, is + 0.000071 gram for every apparent gram of salt. A vacuum correction of — 0.000031 gram was applied to every apparent gram of silver.

[1] Baxter and Hines: *Am. Chem. J.*, **31**, 222.

Weight of silver iodide in vacuum. Grams.	Weight of water displaced in vacuum. Grams.	Density of silver iodide. 25°/4°.
15.5871	2.7590	5.650
14.5141	2.5652	5.658
16.3685	2.8853	5.673
	Average,	5.660
21.5876	3.8017	5.678
16.7274	2.9505	5.669
	Average,	5.674[1]

The platinum-plated brass weights were twice carefully standardized to hundredths of a milligram, and the two sets of corrections agreed to within 0.02 mg. in every case. Two short-armed Troemner balances, sensitive to a fiftieth of a milligram with a load of 50 grams, were used in the work. All weighings were made by substitution. In the case of the Gooch crucible a platinum tare, and in the case of the porcelain crucibles, porcelain tares were used.

In the following table are given the results of all the syntheses which were completed without accident. The atomic weight of silver is assumed to be 107.930 in the calculations.

THE ATOMIC WEIGHT OF IODINE.

Preliminary Series. Ag : AgI.

No. of analysis.	Sample of iodine.	Weight of silver in vacuum. Grams.	Weight of silver iodide in vacuum. Grams.	Loss on fusion. Gram.	Weight of silver from filtrate. Gram.	Weight of silver iodide and asbestos from filtrate. Gram.	Corrected weight of silver iodide in vacuum. Grams.	Atomic weight of iodine.
1	I	5.23123	11.38079	0.00030	.....	0.00482	11.38531	126.970
2	I	3.57039	7.77026	not fused.	.....	0.00007	7.77033	126.961
3	I	4.60798	10.02751	0.00047	.....	0.00100	10.02804	126.951
4	I	4.52467	9.84838	0.00036	.....	0.00020	9.84822	126.986
5	I	4.65256	10.14605	0.00062	.....	0.00048	10.14591	126.930
					Average			126.960

[1] The values for the density of silver iodide found by other experimenters are as follows:

Boullay: *Ann. chim. phys.* (2) **43**, 266 (1830)..... 5.614
Karsten: *J. Chem. Phys.*, **65**, 417 (1832)..... 5.026
Filhol: *Ann. chim. phys.* (3) **21**, 417 (1847)..... 5.500
Schiff: *Ann. Chem. Pharm.*, **108**, 21 (1858) 5.35
H. St. Clair Deville: *Compt. Rend.*, **64**, 325 (1867) ..... 5.687 at 0°
Schroeder: *Ann. Chem. Pharm.*, **192**, 295 (1878) ..... 5.650 to 5.718

No. of analysis.	Sample of iodine.	Weight of silver in vacuum.	Weight of silver iodide in vacuum.	Loss on fusion.	Weight of silver from filtrate.	Weight of silver iodide and asbestos from filtrate.	Corrected weight of silver iodide in vacuum.	Atomic weight of iodine.
			Final Series. Ag : AgI.					
6	I	4.77244	10.38668	0.00020	0.00033	0.00050	10.38698	126.975
7	I	4.82882	10.50876	0.00035	0.00053	0.00140	10.50981	126.977
8	II,1	4.04262	8.79718	0.00058	.....	0.00095	8.79755	126.947
9	II,1	1.64711	3.58503	0.00020	0.00015	0.00032	3.58515	126.994
10	II,2	4.86054	10.57440	0.00122	0.0025	lost.	10.57318	126.972
11	II,2	4.83482	10.52213	0.00044	0.00032	0.00072	10.52241	126.967
12	II,3	4.97120	10.81696	0.00025	0.00052	0.00129	10.81800	126.940
13	II,3	3.53858	7.70139	0.00038	0.00017	0.00035	7.70136	126.969
14	II,3	3.89693	8.48181	0.00026	0.00012	0.00032	8.48187	126.985
15	II,4	5.33031	11.59785	0.00034	0.00185	0.00360	11.60111	126.973
16	II,4	5.08748	11.07231	0.00035	0.00017	0.00063	11.07259	126.973

Average 126.970

Average, rejecting analysis 12 ..... 126.973

Average of analyses with Sample I 126.976

Average of analyses with Sample II, Fraction 1 ..... 126.971

" " " " " " " 2 ..... 126.970

" " " " " " " 3 ..... 126.977

" " " " " " " 4 ..... 126.973

The results tabulated in the preliminary series were undoubtedly less accurate than those of the final series, since it was in these analyses that experience in handling silver iodide was gained. Hence these analyses are collected by themselves. In the final series the rejection of Analysis 12 seems justifiable, since two other analyses made with the same material yielded results in close agreement and considerably higher than that of Analysis 12.

From an examination of this table two important deductions may be drawn. First, there can be little doubt of the identity of the different samples of iodine, for the extreme averages of the results from the various samples differ by only 0.007 of a unit. The variation in the values from the analysis of Sample II, Fraction 1, was undoubtedly due in the case of Analysis 8 to lack of experience in manipulating silver iodide, for this analysis was the first one to be completed in the final series, and in the case of Analysis 9, to the small quantity of available material. One may conclude without hesitation that, in the material examined in this investigation at least, no new halogen existed.

The second important deduction is that the atomic weight of iodine is evidently very slightly greater than 126.973, for most of the experimental errors, such as loss of silver iodide, or loss of iodine by the silver iodide, would have caused the result to be too low.

Part II.

THE RATIO OF SILVER TO IODINE.

The ratio of silver to iodine was next investigated. The problem of obtaining iodine in a *dry* state presented most difficulties in this portion of the research, and was finally solved as follows: Iodine which had been prepared in the same way as Sample I, was first freed from the greater part of the water which it contained by exposure to concentrated sulphuric acid, which had been boiled to remove every trace of hydrochloric acid. It was then sublimed from a crystallizing dish to the bottom of a glass dish half filled with water, which covered the crystallizing dish. In this way the greater part of the "included" moisture must have been eliminated. The sublimed crystals were finally again sublimed in a current of pure dry air from a porcelain boat contained in a hard glass tube into the weighing-tube. This weighing-tube was about 10 cm. long and 15 mm. in diameter, and was drawn down to less than half this diameter at both ends. Glass stoppers were ground into both ends of the tube. The air was purified and dried by passing over beads moistened with a solution of silver nitrate, then over sodium carbonate, and finally over three feet of beads moistened with concentrated sulphuric acid, all in an apparatus made entirely of glass and connected with the sublimation tube by means of a ground glass joint. During the final sublimation of the iodine, the end of the hard glass tube, which had been drawn down to small diameter, was inserted into one end of the weighing-tube. After the weighing-tube had been filled, the glass stoppers were inserted, the tube was carefully wiped with a slightly damp "chemically clean" cloth, and was allowed to stand in a desiccator for some time. It was then weighed. Needless to say the weighing-tube had been originally treated as above before being weighed empty. Both weighings were made with a counterpoise exactly similar to the weighing-tube.

In all but one of the experiments the weighing-tube was broken during the solution of the iodine, so that it was impossible to weigh the tube after the experiment, and determine how much the glass

was attacked by the warm iodine. In one experiment, however, a loss in weight of 0.00032 gram was found. Whether or not this change was accompanied by the evolution of a gas, the loss in weight must have been at least partially due to combination of the iodine with the alkaline metals of the glass, with the formation of soluble iodides which were dissolved by the solution of sulphurous acid. Hence the error must have been considerably less than 0.3 mg., if, as was necessarily the case owing to breakage of the tubes, the first weight of the tube was used in determining the weight of the iodine.

Immediately after being weighed, in order to avoid loss by volatilization, the iodine was converted into hydriodic acid by means of pure sulphurous acid. This acid was made by heating sulphuric acid with metallic copper and collecting the sulphurous oxide in water, and then distilling the sulphurous oxide from the solution into the purest water. During this distillation any trace of halogen acid which might have had its source in either copper or sulphuric acid must have been completely eliminated, for it must have been almost wholly in the ionized condition.

A considerable quantity of this sulphurous acid was poured into one of the precipitating flasks, and the weighing-tube, containing the iodine, was introduced, after the lower stopper had been allowed to drop out of the tube into the flask. The sulphurous acid immediately sealed the open end of the tube so that no iodine vapor could escape. The other stopper was then removed by means of a platinum wire, the wire rinsed into the flask, and the flask quickly closed by means of its glass stopper. Solution of the iodine in the sulphurous acid was hastened by gently agitating the flask. Any iodine vapor which escaped from the tube must have been instantly converted into hydriodic acid. After sufficient time had been allowed for every trace of this hydriodic acid to be absorbed by the solution, the flask was opened and the solution transferred to another precipitating flask, and a slight excess of the purest ammonia added. When iodine is dissolved in a large excess of sulphurous acid the solution becomes colored yellow, owing to the formation of an iodide of sulphur,[1] and, upon standing, this solution may deposit sulphur. Since the solution was made alkaline with ammonia as soon as the iodine was dissolved, with the complete disappear-

[1] Dammer: *Handb. d. anorg. Chem.*, **1**, 557.

ance of the color and without the formation of the slightest trace of a precipitate, no danger was to be feared from this source.

From the weight of the iodine, the weight of silver necessary exactly to combine with it was calculated. This silver was weighed out and dissolved in nitric acid, as described previously in this paper. The solution was diluted until not stronger than 1 per cent. and was added slowly to the already dilute solution of ammonium iodide in the precipitating flask. The flask was shaken for some time, and was then made acid with a considerable excess of nitric acid. Long-continued shaking, followed by several days' standing, yielded a clear supernatant solution. Twenty-five cc. portions of this solution were pipetted into nephelometer tubes and were tested with cubic centimeter portions of hundredth-normal silver nitrate and hydriodic acid solutions in a nephelometer.[1] If an excess of either iodine or silver was present, the deficiency of the other was made up in the remaining solution by addition of standard silver nitrate or hydriodic acid until the exact end-point was reached. It was never necessary to add more than 0.1 mg. of either iodine or silver, so that the liquid removed from the flask for the tests could be neglected. This end-point is very sharp in the case of silver and pure iodine, for so little silver iodide is dissolved that the two nephelometer tubes remain almost absolutely clear. An excess of a 0.1 mg. of silver in a liter of solution is easily detected. This almost complete lack of opalescence in the nephelometer tubes is strong evidence of the absence of even a trace of either chlorine or bromine in the iodine, for silver chloride or bromide, on account of their greater solubility, would have produced much more marked precipitates.

The specific gravity of solid iodine was assumed to be 4.933;[2] hence a vacuum correction of +0.000102 was applied to every apparent gram of iodine.

THE ATOMIC WEIGHT OF IODINE.

Ag : I.

Number of analysis.	Weight of silver in vacuum. Grams.	Weight of iodine. in vacuum. Grams.	Atomic weight of iodine.
17	5.54444	6.52288	126.977
18	6.27838	7.38647	126.979
19	4.57992	5.38814	126.976
		Average,	126.977

[1] Richards and Wells: *Am. Chem. J.*, **31**, 235.

[2] Ladenburg: *Ber. d. chem. Ges.*, **35**, 1256.

As was to be expected, the average of this series is slightly higher than that of the previous one, and undoubtedly represents very closely the true value of the atomic weight of iodine. Nevertheless, the investigation was not allowed to rest at this point.

Part III.

The Ratio of Silver Iodide to Silver Chloride.

In any atomic weight investigation it is extremely desirable to obtain the value sought by reference to as many different well-known atomic weights as possible. The method of heating silver iodide in a current of chlorine, which has already been used by Berzelius and Dumas, as well as by Ladenburg, furnishes the ratio between iodine and chlorine, and seemed capable of yielding trustworthy results, for since the silver halides fuse at a comparatively low temperature, there is no possibility of inclusion of silver iodide by the silver chloride formed in the reaction, and hence there is certainty that the reaction will be complete.

First, silver iodide was prepared by precipitating an ammoniacal solution of the purest ammonium iodide (Sample I) with a solution of recrystallized silver nitrate. In this operation a slight excess of ammonium iodide was used. The precipitate was well washed with 1 per cent. nitric acid, rinsed with water, and was collected on a Gooch crucible with the use of a disk of filter-paper instead of an asbestos mat. In this way contamination of the precipitate with asbestos shreds was avoided. The silver iodide was finally dried in an air-bath at about 100° C. for at least eight hours. After removal of the filter-paper, those portions of the precipitate which had come in contact with the filter-paper were cut away with a clean knife. Next the substance was fused in a weighed crucible protected from the flame by a very large crucible. While the silver iodide was fused, a small quantity of the purest iodine was placed upon the lower side of a second crucible cover, and this cover was substituted for the one which had been weighed with the crucible. The iodine immediately vaporized and the silver iodide was thus fused in an atmosphere contaning iodine vapor. Finally the cover was removed, so that the uncombined iodine escaped from the crucible, and the salt was kept fused, covered with the original crucible cover, until it was certain that all excess of iodine had been eliminated. That no excess of iodine

was retained by the silver iodide was readily shown in one experiment with 18 grams of salt by reheating the salt to its fusing-point and reweighing. A loss in weight of only 0.00003 gram resulted.

After the silver iodide had been weighed it was heated in a current of chlorine. This gas was generated by dropping concentrated hydrochloric acid upon manganese dioxide, and it was purified and dried by bubbling through water and passing through a three-foot tube filled with beads moistened with concentrated sulphuric acid. Traces of bromine or iodine in the chlorine would have been no disadvantage, and it is inconceivable that it should have contained fluorine. In order to prevent spattering of the fused salt from the crucible, a perforated porcelain disk, which fitted the crucible half-way between the bottom and the top, was placed in the crucible. This disk was always weighed with the crucible. The chlorine was conducted into the crucible by means of a small hard glass tube, which passed just through the perforated cover of a Rose crucible. The apparatus for generating chlorine was constructed wholly of glass with the exception of the joint between this hard glass tube and the drying tube. The chlorine did not come in contact with the rubber tube used in making the connection tight, however, for the hard glass tube telescoped into the drying tube for some distance and the joint was sealed with concentrated sulphuric acid. In order to avoid volatilization of the silver salts, the heat applied was very gentle and only sufficient to fuse the silver chloride. Even at this temperature the iodine was rapidly replaced. Heating in chlorine was continued some time after the color of the iodine vapor had ceased to be visible. Then the Rose cover was replaced by the ordinary cover and the silver chloride was kept fused for several minutes, with occasional lifting of the cover, so as to drive off any chlorine which might have been dissolved by the fused salt. Although fused silver chloride, when cooled in chlorine, dissolves this gas very appreciably, no evidence was found that any remained in the solidified salt when it was heated for a short time in air. In one experiment, 18 grams of the chloride, after the usual treatment, were re-fused in air with a loss in weight of only 0.00002 gram. The same chloride, when fused and cooled in chlorine, gained 5 mg.

It was soon discovered that a porcelain crucible, when used for the conversion of silver iodide into silver chloride, gradually gained in weight. In the first experiment this gain was over $\frac{3}{4}$ mg., and in several subsequent experiments with the same crucible amounted to slightly less than a milligram in each case. This gain did not take place to the slightest extent when the crucible was heated alone in chlorine, nor after the reaction was complete, for the weight of the crucible and silver chloride very soon became constant. Probably it was due partially to solution of the silver salt in the glaze, as was shown by slight discoloration on the bottom of the crucible. Possibly, however, it was caused by the attacking of the glaze by the "nascent" chlorine and iodine set free in the process, perhaps with evolution of oxygen. At any rate too great an uncertainty existed as to the weight of the crucible at the end of the experiment. Accordingly, quartz crucibles were next employed for the same purpose. These crucibles behaved in an ideal fashion, for they remained practically constant in weight through the process. It was only necessary to rotate the crucibles during the solidification of the fused salts in order that the salt might solidify in a thin layer on the sides of the crucible. Neglect to do this almost invariably resulted in the cracking of the crucible.

After the first weighing of the crucible it was again heated in chlorine for an hour, and again cooled and weighed. In no case did a loss in weight of more than 0.1 mg. take place, showing both that the iodine was completely replaced, and that no silver chloride had volatilized.

Four determinations (Analyses 20 to 23) were completed with quartz crucibles in the manner described. Two more determinations (Analyses 24 and 25) were made by heating silver iodide first in a current of carbon dioxide and bromine, and then in chlorine. The weight of the silver bromide was obtained, but, although the results for the atomic weight of iodine calculated from the weight of the bromide agreed closely with those obtained by the other methods, on account of some uncertainty as to the purity of the bromine, these results are withheld until the experiments can be repeated. The only possible impurity in the bromine, chlorine, would not affect the final weight of the silver chloride.

At the time these experiments were performed the atomic

weight of chlorine was thought to be 35.456. The atomic weight of iodine calculated from the ratio between silver iodide and silver chloride, using this value for chlorine, was very close to 126.96 in every case, which is considerably lower than the results obtained from the other two methods. At about this time, however, Richards and Wells, working upon the atomic weight of sodium in this laboratory, found that the atomic weight of chlorine is in reality 35.467.[1] In the following table the results are calculated upon this basis.

The specific gravity of silver chloride was assumed to be 5.56 as recently determined by Richards and Stull in this laboratory, and accordingly a vacuum correction of +0.000075 was applied to every apparent gram of salt.

THE ATOMIC WEIGHT OF IODINE.

AgI : AgCl.

Ag = 107.930 Cl = 35.467

Number of analysis.	Weight of silver iodine in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of iodine.
20	9.26860	5.65787	126.980
21	6.72061	4.10259	126.974
22	11.31825	6.90912	126.977
23	10.07029	6.14754	126.969
24	13.65457	8.33538	126.975
25	17.35528	10.59457	126.973
	Average		126.975
	From ratio Ag : AgI		126.973
	From ratio Ag : I		126.977
	Average from all three ratios		126.975

The close agreement of the average of the last series with the averages of the first two series leaves no doubt that the atomic weight of iodine is very close to the final average of all three series, 126.975. Incidentally this agreement is additional evidence in favor of Richards and Wells's new value for the atomic weight of chlorine, 35.467. Further work is under way upon the atomic weight of iodine, with the purpose of determining the ratio between iodine and silver iodide, and the ratio between all the halogens, as described upon page 1592 of this paper.

In discussing the bearing of this investigation upon the results of earlier work by other chemists, the experiments of Millon upon

[1] This investigation will soon be published.

silver and potassium iodates,[1] and of Berzelius[2] and Dumas,[3] who converted silver iodide into silver chloride, may be disregarded, since at the time the analyses were made quantitative analysis was in its infancy. Marignac's value for the atomic weight of iodine, 126.85, obtained from the titration of weighed amounts of silver with potassium iodide,[4] and from syntheses of silver iodide from weighed quantities of silver, may be accounted for by the supposition that the iodine used in the experiments was not pure. To explain Stas's[5] low value, 126.85, is a difficult matter. His iodine was purified by two different methods, *i. e.*, by once precipitating or distilling the iodine from a strong solution of potassium iodide, and by precipitation of nitrogen iodide. A third sample was purified by both methods. Since the material purified by each of the two methods gave identical results with that purified by both methods, it is inconceivable that either method of purification should not have been effective. Impurity in the silver or loss of silver iodide are improbable causes of the discrepancy, for the weight of the silver iodide produced was equal to the sum of the weights of the silver and iodine employed. Richards and Wells have recently shown, however, that Stas was not infallible, and, in fact, was capable of making serious mistakes, such that his value for the atomic weight of sodium was 0.2 per cent. too high, and that for the atomic weight of chlorine 0.03 per cent. too low, so that it is not at all surprising to find that here also his work was faulty in some undiscovered particular.

Ladenburg's result,[6] when calculated from the true value of the atomic weight of chlorine, becomes 126.978, which agrees very closely with the value deduced in this paper. His determinations were affected by several small errors, so that the close agreement is somewhat the result of chance. In the first place, porcelain crucibles, as has been pointed out before, gain in weight when used for the conversion of silver iodide into silver chloride, so that the weight of the silver chloride is somewhat uncertain. Furthermore, Ladenburg did not fuse the silver iodide before weighing it. Although Stas states that silver iodide may be

[1] *Ann. chim. phys.* (3), **9**, 400 (1843).
[2] *Ibid.*, (2) **40**, 430 (1829).
[3] *Ann. Chem. Pharm.*, **113**, 28 (1860).
[4] Berzelius' "Lehrbuch," 5th ed., **3**, 1196.
[5] *Œuvres Complètes* **1**, 548.
[6] *Ber. d. chem. Ges.*, **35**, 2275.

completely dried without fusion, his experiments show a loss in weight on fusion of 0.002 per cent., while the average loss on fusion, as given on pages 1585 and 1586 is about 0.004 per cent. Moreover, Ladenburg's method of purifying silver iodide, by washing the precipitated salt with ammonia, could hardly be expected to remove last traces of silver chloride and silver cyanide "included" by the precipitate. These errors are all so small that they would not affect the second place of decimals. However, Ladenburg's, Scott's,[1] and Köthner and Aeuer's work all afford confirmation that the atomic weight of iodine is undoubtedly much higher than has been usually supposed.

The results of the research are, then, as follows:

(1) The atomic weight of iodine is found to be 126.975 (O = 16.000).

(2) Richards and Wells's value for the atomic weight of chlorine, 35.467, is confirmed.

(3) The existence of an element of the halogen family of higher atomic weight than iodine is shown to be improbable.

(4) The specific gravity of pure fused silver iodide is found to be 5.674 at 25° referred to water at 4°.

I am indebted to the Cyrus M. Warren Fund for Research, in Harvard University, for platinum vessels, quartz crucibles and balance, all indispensable in the research.

CHEMICAL LABORATORY OF HARVARD COLLEGE,
CAMBRIDGE, MASS., August 6, 1904.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 89.]

THE USE OF THE ROTATING ANODE IN ELECTRO-ANALYSIS.

BY EDGAR F. SMITH.

Received September 21, 1904.

THE results obtained by Exner, in this laboratory, with a rotating anode in the electrolytic precipitation of metals led to further study along the same line. Thus, Ashbrook succeeded in effecting a number of separations reducing the time factor, in every instance, very considerably. Ingham exhaustively investigated the precipitation of zinc from various electrolytes, show-

[1] *Proc. Chem. Soc.*, **18**, 112.

ing also how this metal could be quickly determined in its most frequently occurring ore, thereby making a very definite and valuable contribution to technical and mineral analysis.

To still further emphasize the advantages arising from the use of a rotating anode in electro-analysis, Ingham demonstrated the possibility of estimating nitric acid in the alkali nitrates with great accuracy in thirty minutes.

It is only fair to say that Exner in no sense exhausted the possibilities of metal precipitation, aided by the rotating anode. Other workers, in this laboratory, have followed him, giving more attention to details, thus gradually accumulating a vast amount of data relating to the various electrolytes and to the conditions most favorable for successful experimentation. That is the merit, in large measure, of Ingham's study of zinc. The facts presented in the present communication are of a similar character. It is our purpose to continue studies in this direction, and also to add to the separations already accomplished by Ashbrook.

The data here presented in regard to the estimation of nickel and cobalt electrolytically will be found decidedly helpful in many ways.

I. Determination of Nickel in Various Electrolytes.

By George H. West.

It is not necessary to enumerate here the many recommendations made at various times by chemists for the electrolytic determination of this metal, but we will merely present the conditions under which the work was done, and give the results obtained by us. Neither is it necessary to occupy space with a description of the apparatus employed in arriving at these results, beyond stating that it was identical with that previously used by Exner, Ingham, and Ashbrook in this laboratory.

The dilution of solution in the various electrolytes ranged from 100 to 125 cc., which represented a cathode surface of 100 sq. cm. The speed of the anode varied from 500 to 650 revolutions per minute. The deposits of nickel were crystalline and gray in color from solutions in which there was an excess of ammonia, while from acid solutions the metal was brilliant and exceedingly metallic in appearance—closely resembling the platinum dish. Whenever peroxide appeared on the rotating anode it was made to disappear, in ammoniacal solutions, by the addition of more ammonia water

to the electrolyte, and when in acid solutions by lowering the current toward the end of the decomposition, and after a few minutes again increasing it, or by introducing into the acid liquid a few drops of a mixture consisting of 5 cc. of glycerol, 45 cc. of alcohol and 50 cc. of water. Pure nickel sulphate was the salt used. To indicate the rate of precipitation the results are plotted in each instance. In this form they become highly instructive.

(A) AMMONIUM ACETATE ELECTROLYTE.

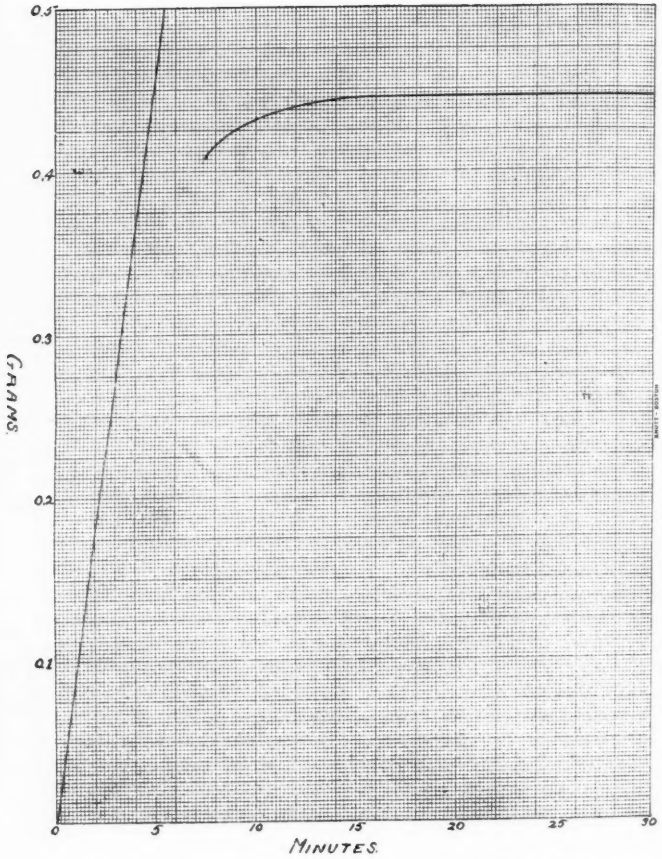
Expt. No.	Nickel present. Gram.	Ammonia (sp. gr. 0.94.). cc.	Acetic acid (26 per cent). cc.	Amperes.	Volts.	Time. Minutes.	Nickel found. Gram.
1	0.4444	20	10	5	4.7	16	0.4438
2	0.4444	25	10	5	4.6	15	0.4404
3	0.4444	20	10	5	4.6	12½	0.4409
4	0.4444	25	10	5	4.6	15	0.4436
5	0.4444	25	10	5	4.6	20	0.4444
6	0.4444	25	10	5	4.6	7½	0.4082
7	0.4444	25	10	5	4.6	10	0.4326
8	0.4444	25	10	5	4.6	30	0.4454

Experiments 1, 4 and 5 record the most favorable conditions. Reference to Exner's experience with this same electrolyte shows that he precipitated about 0.25 gram of nickel completely in ten minutes. There was no anodic deposition in the above experiments, which are graphically shown in Fig. 1.

(B) SODIUM ACETATE ELECTROLYTE.

Nickel present. Gram.	Sodium acetate, 1 cc. = 0.1 gram salt. cc.	Acetic acid (26 per cent.). cc.	Amperes.	Volts.	Time. Minutes.	Nickel found. Gram.
0.4431	30	0.25	5	7.5	7½	0.4028
0.4431	30	0.25	5	7.5	10	0.4256
0.4431	30	0.25	5	7.0	15	0.4306
0.4431	30	0.40	5	7.0	20	0.4431
0.4431	30	0.25	5	7.5	20	0.4422
0.4431	30	0.25	5	7.0	20	0.4429
0.4431	30	0.25	5	7.5	25	0.4432
0.4431	30	0.25	5	7.5	30	0.4432
0.4431	30	0.25	5	7.5	30	0.4432

It is evident that the precipitation here was slower than in the preceding series of experiments. The solution, however, in this instance was acid, and under such conditions more time was invariably required for complete precipitation. In each of these



NICKEL FROM AMMONIUM ACETATE ELECTROLYTE

Fig. 1.

determinations there was also present 0.5 cc. of the glycerol—alcohol mixture. It effectually prevented any deposition upon the anode. The graphic representation of the results is given in Fig. 2.

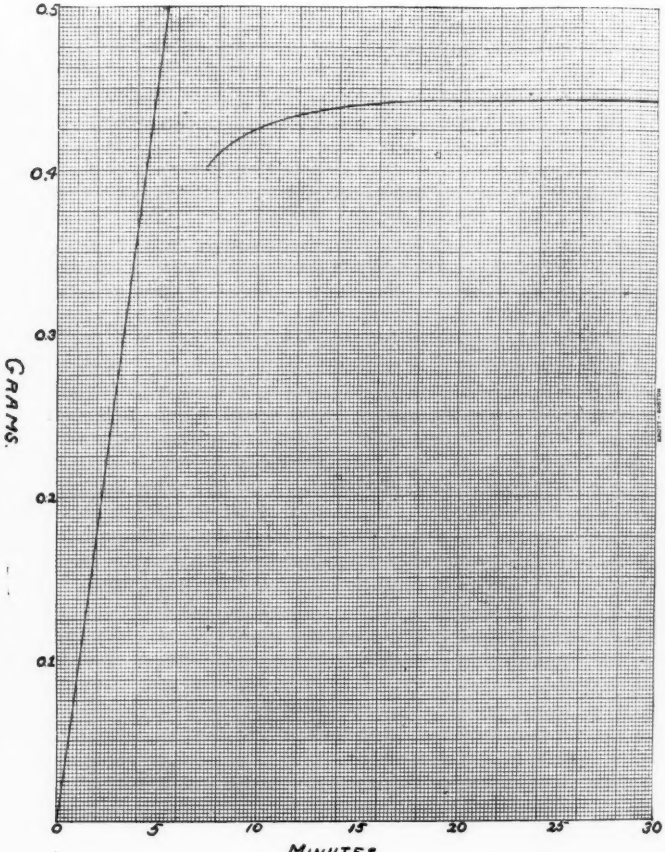
(C) AMMONIA AND AMMONIUM SULPHATE ELECTROLYTE.

This is, of course, the time-honored solution from which nickel has been deposited by the current for analytical and other purposes. Exner gave it some attention in connection with the rotating anode. The appended results supplement and complete his very nicely. A study of the graphic representation in Fig. 3 will prove interesting and instructive.

No.	Nickel present. Gram.	$(NH_4)_2SO_4$. Grams.	NH_4OH (sp. gr. 0.94). cc.	Amperes.	Volts.	Time. Minutes.	Nickel found. Gram.
1	0.2522	1.2	20	4	5.5	1	0.0538
2	0.2522	1.2	20	4	5.5	2	0.0957
3	0.2522	1.2	20	4	5.5	3	0.1474
4	0.2522	1.2	20	4	5.5	4	0.1733
5	0.2522	1.2	20	4	5.5	5	0.2102
6	0.2522	1.2	20	4	5.5	7½	0.2444
7	0.2522	1.2	20	4	5.5	10	0.2493
8	0.2522	1.2	20	4	5.5	15	0.2522
9	0.2522	1.2	20	4	5.5	20	0.2531
10	0.2522	1.2	20	4	5.5	30	0.2525
11	0.5050	1.2	25	4	5.5	1	0.0571
12	0.5050	1.2	25	4	5.5	2	0.1164
13	0.5050	1.2	25	4	5.5	3	0.1549
14	0.5050	1.2	25	4	5 5	4	0.2000
15	0.5050	1.2	25	4	5.5	5	0.2510
16	0.5050	1.2	25	4	5.5	7½	0.3580
17	0.5050	1.2	25	4	5.5	10	0.4450
18	0.5050	1.2	25	4	5.5	15	0.5007
19	0.5050	1.2	25	4	5.5	20	0.5050
20	0.5050	1.2	25	4	5.5	30	0.5052
21	0.5050	1.2	25	5	7	7½	0.4518
22	0.5050	1.2	25	5	7	10	0.4876
23	0.5050	1.2	25	5	7	15	0.5042
24	0.5050	1.2	25	5	7	20	0.5049
25	0.5050	1.2	25	6	8.5	20	0.5046
26	1.0100	1.2	30	5.2	6.5	25	1.0093
27	1.0100	1.2	30	5.2	6.5	25	1.0093

(D) FORMATE ELECTROLYTE.

These results represent the first study of nickel in the presence



NICKEL FROM SODIUM ACETATE ELECTROLYTE.

Fig. 2.

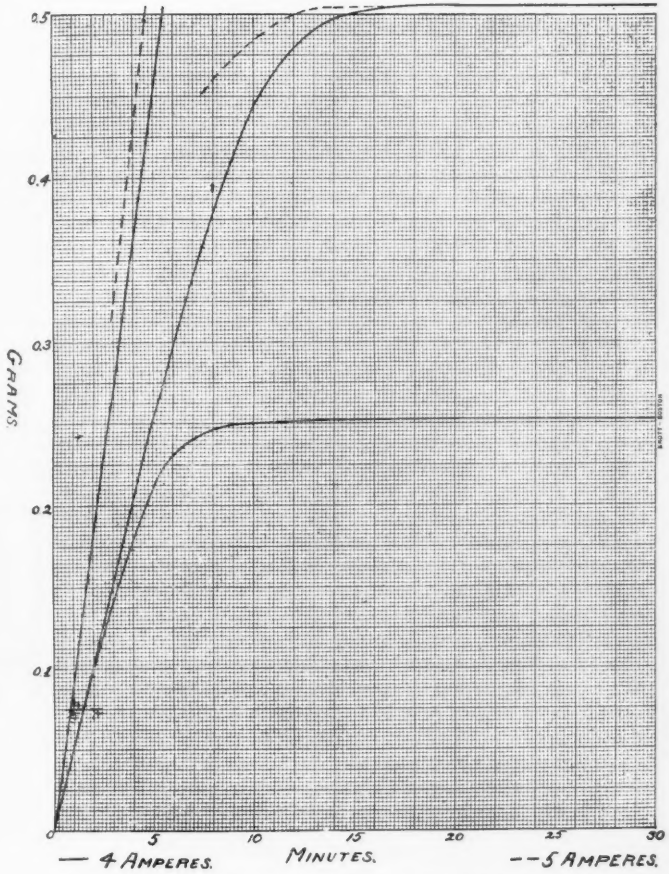

0.5
0.4
0.3
0.2
0.1
GRAMS
0
5
10
15
20
25
30
— 4 AMPERES.
MINUTES.
--5 AMPERES.
NICKEL FROM AMMONIUM SULPHATE ELECTROLYTE.

Fig. 3.

of formic acid, or formates, instituted because of the favorable outcome, under nearly similar conditions, with zinc, by Ingham. They are graphically represented in Fig. 4.

Nickel present. Gram.	NH_4OH. cc.	H.COOH (25 per cent.). cc.	Amperes.	Volts.	Time. Minutes.	Nickel found. Gram.
0.4444	25	10	5	6	7½	0.4214
0.4444	25	10	5	6	10	0.4393
0.4444	20	10	5	6	12½	0.4431
0.4444	20	10	5	6	15	0.4446
0.4444	20	15	5	4	15	0.4443
0.4444	20	10	5	4	15	0.4444
0.4444	20	12	5	4	20	0.4449

(E) SODIUM FORMATE ELECTROLYTE.

Pure sodium carbonate was added to the complete precipitation of the nickel from its sulphate, the precipitate dissolved in excess of formic acid, and the solution electrolyzed. The results were as follows and are graphically recorded in Fig. 5.

Nickel present. Gram.	Na_2CO_3. Grams.	H.COOH (25 per cent.). cc.	Amperes.	Volts.	Time. Minutes.	Nickel found. Gram.
0.4444	5	22	5	4	5	0.2474
0.4444	5	22	5	4	7½	0.3260
0.4444	5	22	5	4	10	0.3688
0.4444	5	22	5	4	15	0.4323
0.4444	5	22	5	4	20	0.4394
0.4444	5	22	5	4	30	0.4448

(F) AMMONIUM LACTATE ELECTROLYTE.

In estimating zinc Jordis[1] recommended its deposition from an ammonium lactate solution in the presence of lactic acid. As this electrolyte had never before been applied, to our knowledge, to nickel, a series of experiments were tried with the results indicated below and graphically represented in Fig. 6.

Nickel present. Gram.	NH_4OH (sp. gr. 0.94). cc.	Lactic acid. cc.	Amperes.	Volts.	Time. Minutes.	Nickel found. Gram.
0.4443	25	2.5	5	6.5–7.5	5	0.3151
0.4443	25	2.5	5	7.5	7½	0.4056
0.4443	25	2.5	5	7.5	10	0.4344
0.4443	25	2.5	5	7.5	15	0.4442
0.4443	25	2.5	5	7.5	15	0.4443
0.4443	25	2.5	5	7.5	20	0.4447
0.4443	25	2.5	5	7.5	20	0.4439
0.4443	25	2.5	5	7.5	22	0.4443
0.4443	25	2.5	5	7.5	25	0.4453
0.4443	25	2.5	5	7.5	30	0.4441

[1] *Ztschr. Elektrochemie*, **2**, 138, 563, 655.

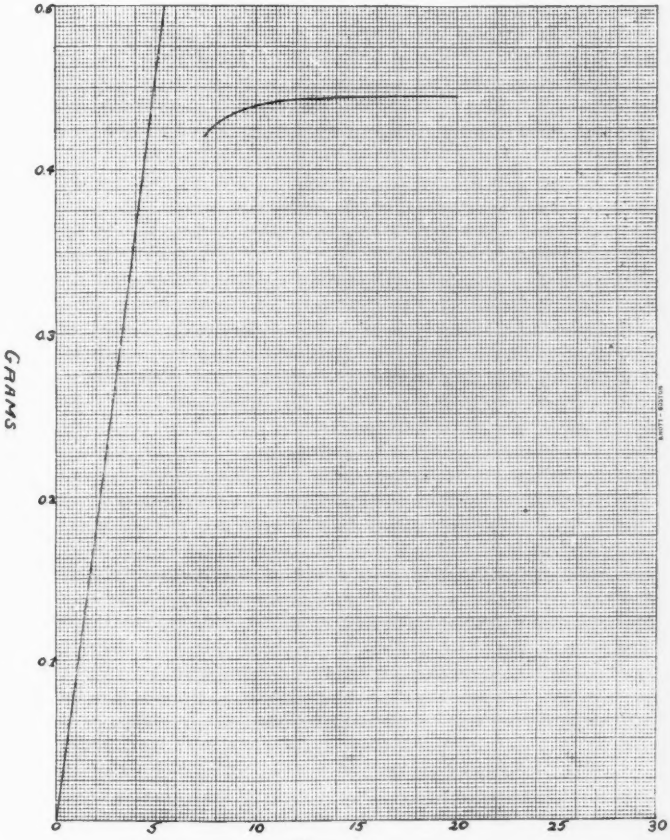
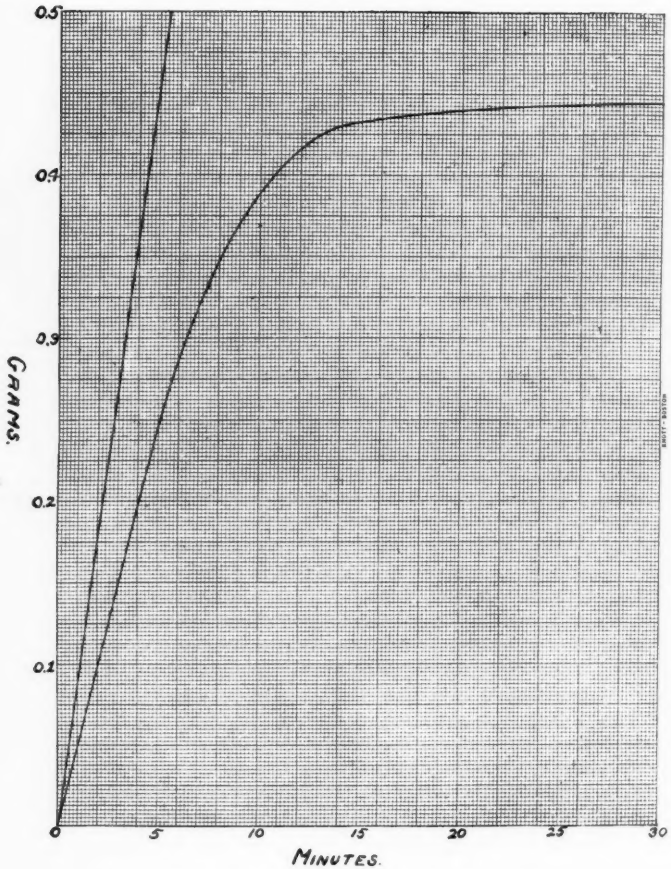

0.5
0.4
0.3
0.2
0.1
GRAMS
0
5
10
15
20
25
30
MINUTES.
NICKEL FROM AMMONIUM FORMATE ELECTROLYTE

Fig. 4.



NICKEL FROM SODIUM FORMATE ELECTROLYTE.

Fig. 5.

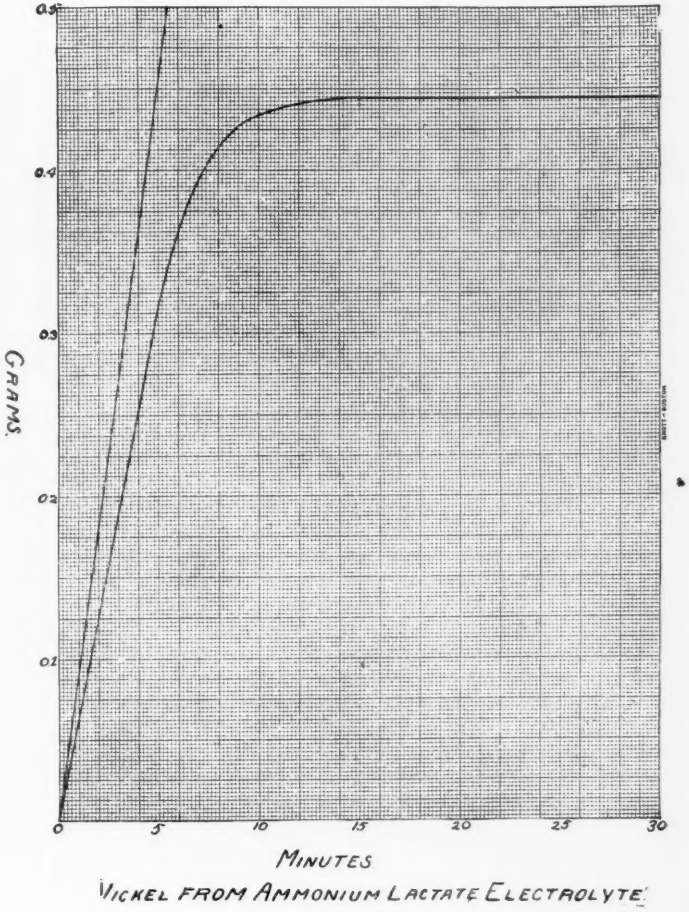

0.5
0.4
0.3
0.2
0.1
GRAMS.
0
5
10
15
20
25
30
MINUTES
NICKEL FROM AMMONIUM LACTATE ELECTROLYTE

Fig. 6.

II. Determination of Cobalt in Various Electrolytes.

By Lily G. Kollock.

The speed of the rotating anode in these trials with cobalt, as well as other details, have been given in the introductory paragraphs, so that its deposition from the various electrolytes may be given without further comment.

(A) Sodium Formate Electrolyte.

To a solution of pure cobalt sulphate, of definite strength, were added 2.5 grams of sodium carbonate and 4 cc. of 94 per cent. formic acid. It was then heated to boiling and electrolyzed with a current of $N.D_{100} = 5$ amperes and 6 volts. After thirty minutes the solution was siphoned from the dish, water being substituted for it. The precipitation of metal was complete. It was so brilliant in appearance that it was hardly distinguishable from the platinum. It may not be superfluous to repeat that in this electrolyte there may occur a slight anodic deposition of peroxide. The glycerol mixture, previously referred to, causes it to disappear or prevents its formation. But it is preferable to lower the current to 1 ampere for a few minutes when the solution has almost lost its color and when the peroxide has disappeared from the anode to restore the current to its original strength. Redeposition of oxide was never observed.

Much formic acid retards the precipitation of the cobalt. If the solution becomes alkaline, the metal is deposited very rapidly and is consequently very spongy. It was found advantageous to add the acid drop by drop from time to time. The quantity of acid indicated in the table was usually all that was necessary in order to insure good results.

Expt. No.	Cobalt taken. Gram.	Sodium carbonate. Grams.	Formic acid. cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
1	0.3535	2.5	3.0	8	6	30	0.3530
2	0.3535	2.5	3.0	8	6	30	0.3535
3	0.3535	4.0	4.5	9	6	35	0.3540
4	0.3535	2.5	4.5	9	6	35	0.3540
5	0.3535	2.5	3.5	10	8	30	0.3530
6	0.3535	2.5	3.5	8	8	30	0.3531
7	0.3525	2.5	3.5	6	6.5	35	0.3535
8	0.3535	2.5	5.0	7	7	40	0.3535
9	0.2635	2.5	3.0	5	5	30	0.2635
10	0.2635	2.5	13.5	7.5	6	30	0.2643
11	0.2635	2.5	14.0	7.5	6	30	0.2630
12	0.2635	2.5	15.0	7.5	6	30	0.2635
13	0.2635	2.4	15.0	7	6	30	0.2630

The formic acid in Expts. 1 to 9 was 94 per cent., and 25 per cent. in those from 10 to 13.

The rate of deposition was studied. The curve was plotted from the following data:

In 5 minutes 0.1470 gram of metal was deposited.
" 7½ " 0.2096 " " " " "
" 10 " 0.2570 " " " " "
" 15 " 0.3066 " " " " "
" 20 " 0.3092 " " " " "
" 25 " 0.3142 " " " " "
" 30 " 0.3152 " " " " "

See Fig. 7.

(B) AMMONIUM FORMATE ELECTROLYTE.

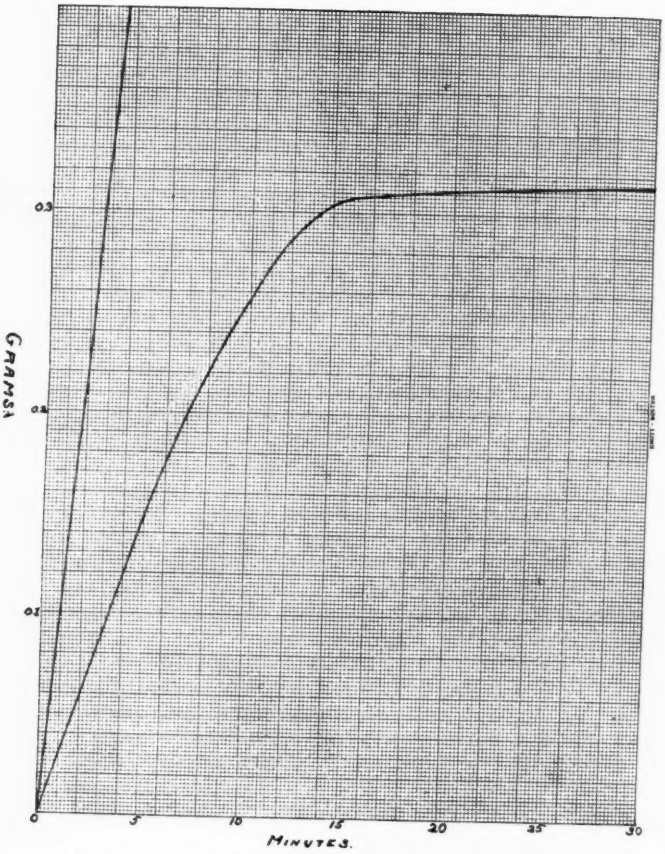
The solution may be alkaline or acid. From the former the metal separates in a compact form, but very dull in appearance, while from an acid solution it separates in a very brilliant form, but more slowly than from an ammoniacal solution. There was little tendency to anodic deposition in this electrolyte. The solution was colorless in fifteen minutes.

Expt. No.	Cobalt present. Gram.	Ammonium hydroxide. cc.	Formic acid (94 per cent.). cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
1	0.1260	20	3	5.5	6	20	0.1265
2	0.3152	25	3	5	6	30	0.3160
2	0.3152	20	3.5	5.5	6	25	0.3152
4	0.3152	20	3.5	7	6.5	20	0.3152
5	0.3152	20	3.5	7	6.5	20	0.3150

(C) AMMONIUM ACETATE ELECTROLYTE.

The deposit of cobalt from this solution was very satisfactory. The metal was brilliant in appearance. The following conditions may be expected to yield excellent results. Peroxide on the anode was not observed in any of these determinations.

Expt. No.	Cobalt present. Gram.	Ammonium hydroxide. cc.	Acetic acid (26 per cent.). cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
1	0.2980	25	10	6	5	20	0.2980
2	0.2980	25	10	6	5	20	0.2980
3	0.2980	25	10	6	5	20	0.2980
4	0.2980	25	10	6	5	20	0.2980
5	0.1324	25	10	5	5.5	25	0.1318
6	0.3310	25	10	6	5	25	0.3304
7	0.3310	25	10	6	5	25	0.3306
8	0.3310	25	10	5	5	25	0.3305
9	0.3310	25	10	5	5	30	0.3310



COBALT FROM SODIUM FORMATE ELECTROLYTE.

Fig. 7.

The conditions of Expt. 1 were observed in getting data for the time curve (Fig. 8).

In	5	minutes	0.2235	gram	of	cobalt	was deposited.
"	10	"	0.2778	"	"	"	"
"	15	"	0.2950	"	"	"	"
"	20	"	0.2980	"	"	"	"
"	25	"	0.2980	"	"	"	"

(D) SODIUM LACTATE ELECTROLYTE.

Cobalt, like nickel, had never been previously studied in an electrolyte containing lactic acid or any of its salts. It proved a most satisfactory solution from which to deposit the metal; at least such was the case while working with the conditions given below. There was no peroxide deposition, and the deposits of metal were adherent and brilliant in appearance. A large excess of lactic acid exerted a retarding influence upon the precipitation.

Expt. No.	Cobalt present. Gram.	Sodium carbonate. Grams.	Lactic acid conc. cc.	Volts.	Amperes.	Time.	Cobalt found. Gram.
1	0.3152	2.2	5	8	5	25	0.3150
2	0.3152	2	5	11	6.5	30	0.3150
3	0.3152	2	4	9.5	5	25	0.3155

(E) AMMONIUM LACTATE ELECTROLYTE.

The results in this solution were, if anything, superior to those obtained in the preceding electrolyte. The liquid became colorless in twelve minutes, but the final traces of cobalt required a little more time for their complete removal. The large amount of ammonium hydroxide was used to increase the conductivity of the liquid.

Expt. No.	Cobalt present. Gram.	Ammonium hydroxide. cc.	Lactic acid. cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
1	0.3152	10	2.5	10	6	30	0.3155
2	0.3310	20	4.5	7.5	6	25	0.3305
3	0.3310	20	4.5	7.5	6	25	0.3310
4	0.3310	30	7	5	6	25	0.3310

In getting data to construct a time curve (Fig. 9), the following conditions were observed: Ten cc. of ammonium hydroxide and 2.5 cc. of concentrated lactic acid were added to the cobalt sulphate solution, which was then electrolyzed with a current of $N.D_{100} = 6$ amperes and 7.5 volts.

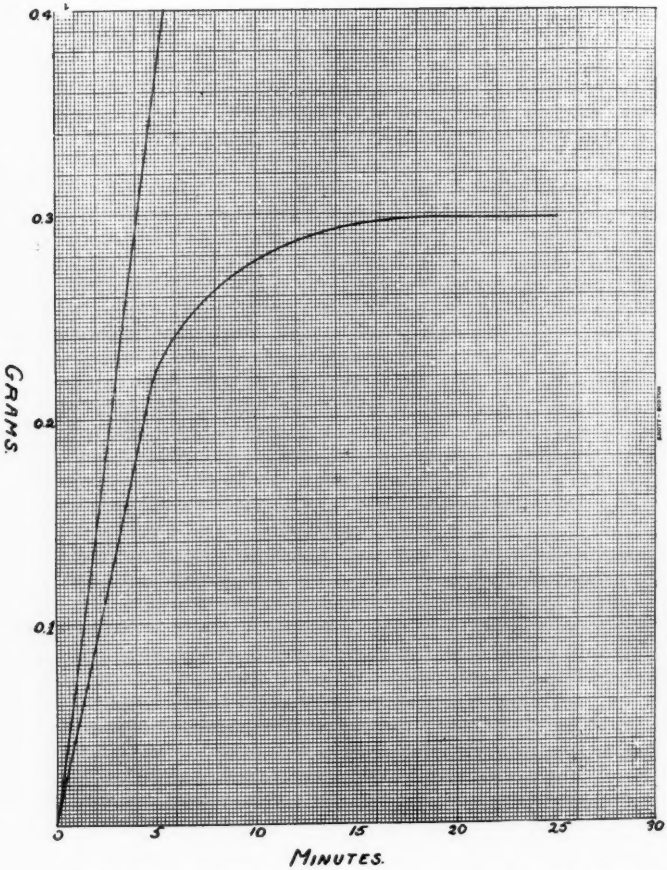
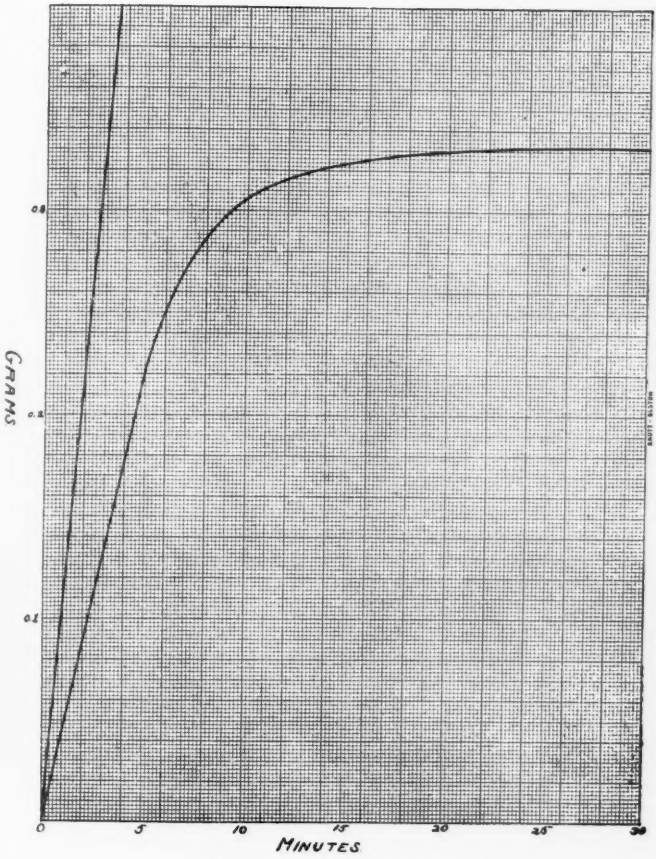

0.4
0.3
0.2
0.1
GRAMS.
0
5
10
15
20
25
30
MINUTES.
COBALT FROM AMMONIUM ACETATE ELECTROLYTE.

Fig. 8.



COBALT FROM AMMONIUM LACTATE ELECTROLYTE.

Fig. 9.

In	5	minutes	0.2215	gram	of	cobalt	was deposited.
"	10	"	0.3060	"	"	"	"
"	15	"	0.3230	"	"	"	"
"	20	"	0.3290	"	"	"	"
"	25	"	0.3310	"	"	"	"
"	30	"	0.3310	"	"	"	"

(F) AMMONIUM SUCCINATE ELECTROLYTE.

In this solution there was a slight deposit on the anode, but it was removed in the manner indicated under the formate electrolytes. A little carbon was observed in the precipitated cobalt. Its quantity was inappreciable.

Expt. No.	Cobalt present. Gram.	Ammonium hydroxide. cc.	Succinic acid. Grams.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
1	0.3310	25	4	5	5.6	30	0.3315
2	0.3310	25	3.5	6	5	25	0.3305
3	0.3310	25	3	6	5	30	0.3309
4	0.3310	25	3	8	6	25	0.3305

The liquid in Expts. 1 and 2 was acid in reaction, while that in Expts. 3 and 4 was alkaline.

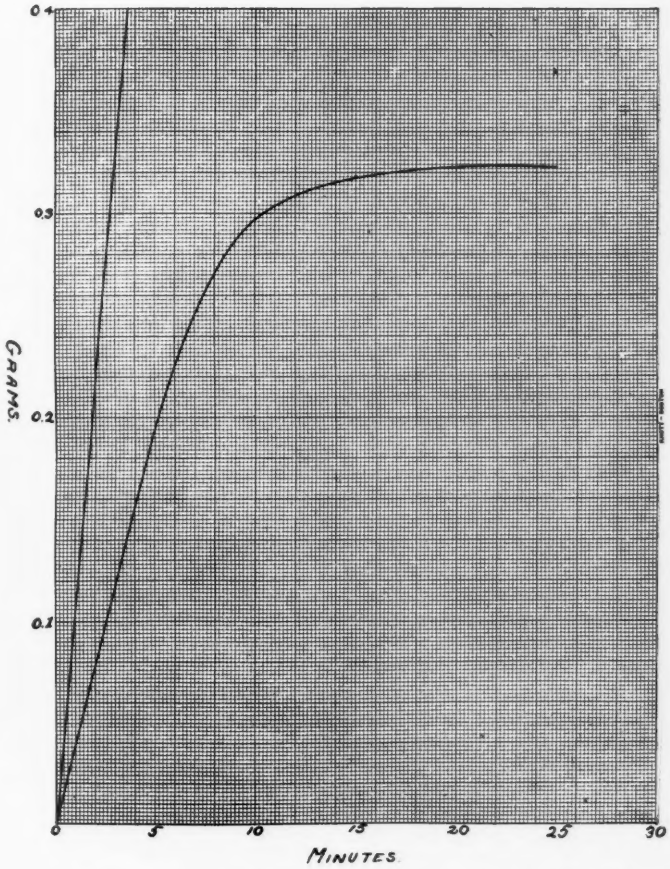
In determining the time curve (Fig. 10) 3 grams of succinic acid and 25 cc. of ammonium hydroxide were added to the liquid which was electrolyzed with a current of $N.D_{100} = 5$ amperes and 8 volts. The results were:

In	5	minutes	0.1935	gram	of	cobalt	was deposited.
"	10	"	0.2975	"	"	"	"
"	15	"	0.3284	"	"	"	"
"	20	"	0.3310	"	"	"	"
"	25	"	0.3310	"	"	"	"

Our experience with sodium succinate was unsatisfactory. There was a great deal of peroxide deposited upon the anode, hence that electrolyte was abandoned.

SEPARATION OF COBALT FROM THE ALKALINE EARTH METALS.

In these separations the metals were present as formates. Care was taken not to have too great an excess of formic acid present, but to add it gradually in order that the solution might continue acid in its reaction throughout the decomposition.



COBALT FROM AMMONIUM SUCCINATE ELECTROLYTE.

Fig. 10.

1. COBALT FROM CALCIUM.

Cobalt present. Gram.	Calcium formate. Gram.	Ammonium hydroxide cc.	Formic acid. cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
0.2135	0.5	10	4	5	6	30	0.2135
0.2135	1	10	4	4.5	6	30	0.2134
0.2135	1.5	10	4.5	4.5	6	30	0.2133
0.2135	1	10	4.5	4.5	6	30	0.2132

2. COBALT FROM STRONTIUM.

Cobalt present. Gram.	Strontium formate. Gram.	Formic acid. cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
0.2040	1.0	5	14	3	25	0.2045
0.2040	1.5	5	14	3	25	0.2135
0.2040	1.5	5	15	3	25	0.2045

In these separations the addition of ammonium formate was omitted. Its presence apparently operated adversely.

3. COBALT FROM BARIUM.

Cobalt present. Gram.	Barium formate. Gram.	Ammonium hydroxide. cc.	Formic acid after neutralization. cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
0.2040	1	10	1	5	6	25	0.2045
0.2040	1.5	10	1	5	6	25	0.2042
0.2040	1	10	1	5	6	25	0.2043

4. COBALT FROM MAGNESIUM.

Cobalt present. Gram.	Magnesium formate. Grams.	Ammonium hydroxide. cc.	Formic acid in excess. cc.	Volts.	Amperes.	Time. Minutes.	Cobalt found. Gram.
0.2040	0.5	5	1	6	5	30	0.2045
0.2040	1	5	1	6	5	30	0.2033

It might seem on first thought that the separations outlined above would proceed without any trouble. Experience showed that it was necessary to observe certain points very carefully, hence the conditions under which we obtained success have been duly recorded.

In addition to the precipitation of metals with a rotating anode experiments have been conducted, in this laboratory, with a mercury cathode.[1] It seemed probable that a rotating anode might be used with advantage, together with the mercury cathode. Accordingly, the beaker with the layer of mercury as described by Smith

[1] This Journal, **25**, 884; **26**, 1124.

and by Myers, in the references cited above, was used. The anode was a spiral of heavy platinum wire, 1 cm. in diameter. It was made to rotate about 600 times per minute. A solution of copper sulphate, when acted upon under these conditions, with a current of 2 amperes and 4 volts, lost its color in fifteen minutes. This led to the following quantitative determinations of copper.

Copper present. Gram.	Volts.	Amperes.	Time. Minutes.	Volume of liquid. cc.	Copper found. Gram.	Separation of poles. cm.
0.2405	10 to 5	0.01 to 2.0	30	40	0.2401	2
0.2405	10 to 5	0.01 to 2.0	20	25	0.2401	1
0.4810	10 to 5	0.01 to 2.0	25	25	0.4805	1

The copper sulphate solution was neutral at the beginning of the decomposition, hence the low current in the early stages of the precipitation. The more concentrated the solution the more rapidly did the metal separate. It seems probable from other experiments that 0.5 gram of copper can be deposited in fifteen minutes. The several trials made with a nickel sulphate solution indicate that from 0.25 to 0.5 gram of that metal can also be precipitated *with a mercury cathode and rotating anode* in about the same period of time.

Mention is here made of these observations as experimentation in this particular direction will be undertaken immediately. Should success attend the same, as there is every reason to believe, one rather expensive factor in electro-analysis will be eliminated, *viz.*, the platinum dish, cone or cylinder.

UNIVERSITY OF PENNSYLVANIA.

COMPOSITION OF THE FOUR SULPHIDES OF MANGANESE.[1]

BY J. C. OLSEN AND W. S. RAPALJE.

Received September 17, 1904.

LITERATURE.

THE composition of the two commonly known sulphides of manganese has been investigated by several workers. The results obtained have been so conflicting that it is impossible to decide from the literature whether either of these sulphides is anhydrous or not, much less to give the exact composition. The reason for this discrepancy, as we shall attempt to show, has been the failure

[1] Read before the New York Section of the American Chemical Society, April 8, 1904.

to recognize the existence of a gray and a red sulphide of manganese.

F. Muck reported that the green sulphide is crystalline (eight-sided plates) and that its composition corresponds to the formula $Mn_2 \begin{matrix} S \\ O \end{matrix} \Big| \begin{matrix} S \\ H_2 \end{matrix}$, and states that he found 7.43 per cent. of water. The theoretical percentage of water, according to the formula given, is 9.38. Muck appears to think that the green sulphide is an oxysulphide containing a molecule of hydrogen sulphide. He seems to have come to this conclusion from the observation that sulphur is given off on heating the sulphide in a stream of hydrogen or carbon dioxide. We have frequently made the same observation, but have attributed it to the presence of free sulphur, which, as is well known, is not completely dissolved by carbon disulphide. Muck prepared the green sulphide by the ammonium oxalate method given on page 1623. He does not give the composition of the pink sulphide.

Alexander Classen,[1] who prepared the green sulphide by digesting the pink sulphide with excess of ammonium sulphide, states that the green modification is anhydrous.

Cleremont and Guiot,[2] who conducted a very extensive investigation on this subject, found that the green sulphide, when dried at 105° in a stream of hydrogen is anhydrous, while the pink variety, dried under the same conditions, contains about 9 per cent. of water. They ignited the material in hydrogen and called the loss water. They do not mention extracting free sulphur before ignition and since samples prepared by us contained from 4 to 14 per cent. of free sulphur they are not justified in stating that the 9 per cent. lost is water.

Völker[3] prepared the pink sulphide by a very laborious method. He passed hydrogen sulphide through a very dilute solution of manganous acetate. He removed the acetic acid liberated by evaporating down the filtrate until the free acid was volatilized. The residue was then diluted with water and hydrogen sulphide again passed. He states that the sulphide so obtained can be washed and dried without decomposition, while that precipitated by means of ammonium sulphide can not. He determined the

[1] *Ztschr. anal. Chem.*, **16**, 319.
[2] *Gazz. chim. ital.*, **23**, 560 (1893).
[3] *Ann. Chem. Pharm.*, **59**, 38.

water by mixing the sample with dry lead carbonate and heating in a glass tube. He obtained the following results:

	Manganese.	Sulphur.	Water.
1.....	60.45	37.68	2.08
2.....	59.09	38.33	2.44

He states that the material varied in color from light to dark red, the first sample being darker than the second.

Antony and Donnini,[1] two Italian chemists, state that "both sulphides are identical in composition and it is erroneous to consider the green sulphide to be an oxysulphide or an anhydride, and the pink a hydrate." They conclude that both sulphides are anhydrous, both are crystalline. The only difference which they can discover, besides the color, is in specific gravity. They find that the green sulphide has a higher specific gravity than the pink modification. They dried the pink sulphide at 70° in an atmosphere of carbon dioxide and extracted the free sulphur with carbon disulphide. Their dried sample was red. On heating a sample to 320° in an atmosphere of carbon disulphide a loss of only 0.21 per cent. was noted.

COMPOSITION OF THE PINK SULPHIDE.

The first sample of the pink sulphide was prepared by precipitating the manganese from a neutral solution of manganous chloride with ammonium sulphide. It was washed by decantation with water containing ammonium sulphide. To prevent oxidation the washing was completed in an atmosphere of hydrogen sulphide, but in about fifteen minutes the precipitate began to change color from pink to green. In forty-five minutes this change was complete. In the subsequent preparations the washing, as well as drying, was carried out in an atmosphere of hydrogen. The hydrogen was carefully freed from oxygen by passing the gas through a red hot tube containing metallic copper.

When filtering off and washing the sulphide, a few minutes' exposure to the air was sufficient to completely convert the material on the surface into the brown sesquioxide. When partially dried, the pink sulphide oxidizes still more rapidly when exposed to the air. One sample had been placed in a desiccator and partially dried by heating in the air-bath after the air had been displaced by hydrogen. On opening the desiccator to remove a large

[1] *Bull. Soc. Chim.*, 1877, p. 353.

amount of water which had collected on its sides, a blue flame was noticed on the partially dried sulphide. On extinguishing the flame the pink material had become white. This material proved to be manganous sulphate. Usually the oxidation produced the brown sesquioxide.

This brown material is readily reconverted to the pink sulphide by treatment with hydrogen sulphide. At first this was done with the dried material. The transformation was quite rapid and was accompanied by a very noticeable increase in temperature. After such a treatment the sulphide was again dried, and the sulphur liberated from the hydrogen sulphide was extracted by means of carbon disulphide. In the later preparations the brown material was removed by allowing a little hydrogen sulphide to pass through the apparatus with the hydrogen. The free sulphur was removed with carbon disulphide as before. No sample of the pink sulphide was obtained which was free from sulphur. The amount present has varied from 4 to 14 per cent.

The drying was conducted on the steam-bath, a partial vacuum of one-half atmosphere being maintained. The drying required from six to eight hours. The bulk of the sulphide decreased, during the drying, to about one-fourth of the original bulk. It was found free from all impurities except sulphur. The dried material is quite stable, requiring no special precautions for its preservation. It can be heated in the air to 100° without oxidation. On heating it to 205° it began to oxidize quite rapidly. It was then heated in an atmosphere of hydrogen to 360°, when it gradually changed to the green modification.

Several samples, prepared in the manner just described, were analyzed. The method employed consisted in extracting the free sulphur with carbon disulphide and then igniting the residue with sulphur in a stream of hydrogen. In this manner the amount of anhydrous manganous sulphide was obtained. The loss was assumed to be water. The following percentages were obtained: 9.30, 6.73, 8.54, 10.58, 8.98, 5.55.

A serious error in this method of determining water was found in the fact that it was impossible to extract all of the free sulphur with carbon disulphide, a portion of it being present in the modification, insoluble in carbon disulphide. We do not believe that this or other errors of analysis account for the great di-

vergence in the results obtained. We believe that the differences were due to the fact that we did not have a product of uniform composition. This became more evident as the work continued.

As the pink sulphide, prepared as just described, showed a tendency during the washing to change color more or less rapidly, another method of preparation was adopted. Instead of precipitating with ammonium sulphide, colorless sodium sulphide was used. Muck, as well as Cleremont and Guiot, have found that in the presence of this reagent the pink modification could not be changed to the green sulphide. The washing and drying were carried out in the same manner as before. The product obtained differed markedly from that previously obtained. It was not pink, but *brick-red*. We consider this product a distinct sulphide of manganese different from the so-called pink sulphide.

The Penfield method of determining water was also adopted. The tubes used were about 8 inches long. Before sealing the end they were heated with the Bunsen burner to dry them. The weighed amount of manganese sulphide was first introduced. Enough anhydrous lead oxide was then introduced to form a layer about ¾ inch long. This amount of lead oxide is sufficient to absorb all of the sulphur given off from the weight of manganous sulphide employed. The water was then expelled in the usual manner by heating with the Bunsen burner. While the tube was cooled with a moist cloth it was fused off and the portion containing the water was weighed. The water was then expelled and the tube again weighed, the difference being the weight of the water. The method was checked by determining the percentage of water in crystallized barium chloride. As the red sulphide contained only a small amount of water, about 7 mg. being the maximum amount weighed, portions of barium chloride containing 7 mg. or less of water were taken. The following results were obtained: 14.54, 14.46, 14.79 per cent., the average being 14.60 per cent., while the theoretical percentage is 14.71.

The percentages of water found in three samples of the red sulphide were 0.74, 0.77 and 0.74. These results agree fairly well with those of Antony and Donnini, who found 0.21 per cent. of water in the "pink" sulphide, which they say was red when dried. Völker found as low as 2.08 per cent. of water and states that this sample was dark red. As he states that his samples varied in

color, his product must have been a mixture, as we soon discovered our "pink" product to have been. Our earlier results agree with those of Cleremont and Guiot, who found about 9 per cent. of water.

It was very gratifying to discover in the next series of preparations the cause of these varying results. This appears to be the presence of a *third or fourth sulphide of manganese* which, from its color, is called the *gray* modification and which contains a considerable amount of water. This sulphide is mentioned by Roscoe and Schorlemmer, who state that its formula is $3MnS.H_2O$, in which the theoretical percentage of water is 6.45. The reference to the literature is erroneous and we have been unable to find the original article. The existence of this sulphide seems to have been overlooked by all the other investigators of the sulphides of manganese.

We obtained it in a sample of the "pink" sulphide which had been exposed during the drying process to more than the usual amount of hydrogen sulphide. This sample was composed of lumps which were gray on one side and red on the other. Some of the pieces which contained the least amount of the red material were selected and the amount of water determined. 2.96 per cent. was found. A portion, which represented a fair average sample of the mixed material, was analyzed and was found to contain 1.76 per cent. of water. It will be observed that this is about two-thirds of the amount present in the impure gray material, and more than twice as much as we have found in the red sulphide. On powdering a portion of this mixed material a product was obtained which has the characteristic flesh color of the so-called pink sulphide of manganese. This sulphide should, therefore, be regarded as composed of varying amounts of the gray and red sulphides of manganese. The various percentages of water found by the other investigators, as well as by ourselves, may be explained by assuming that they had products containing different proportions of these two sulphides. It may also be assumed that the reason why the manganese sulphide produced by sodium or potassium sulphide cannot be converted into the green modification, while that produced by ammonium sulphide will undergo this transformation, is found in the fact that varying amounts of the gray sulphide are present in the latter product.

As we have frequently observed, when the pink precipitate is digested to produce the green sulphide the color first changes to gray. Further effort will be made to obtain the gray modification free from the red and to determine the amount of water present in the pure substance.

COMPOSITION OF THE GREEN SULPHIDE.

The first sample of the green sulphide which was analyzed was prepared by heating the pink modification in an atmosphere of hydrogen to 360°. The temperature was taken by means of an air thermometer. The transformation was quite gradual, being complete after about one hour. The amount of water found in this sample by the Penfield method was 0.97 per cent. Antony and Donnini state that they effected this transformation by heating the pink modification to 320° in a stream of carbon dioxide and that the transformation was complete in one-half hour. Invariably on igniting the pink sulphide with sulphur in a stream of hydrogen a green anhydrous product is obtained.

The remaining samples of the green sulphide which were analyzed were made by the method used in the quantitative determination of manganese given in the next article. The precipitate was washed by decantation and dried in a stream of hydrogen at 100°. This sulphide is much more stable in the air, so that samples have been dried in the air at 100° without the formation of any brown oxide whatever. Sulphur was present in all samples obtained, the lowest percentage found being about 1, while the highest was 4 per cent. The amount of water was determined by Penfield's method, these samples giving 1.18, 1.21 and 0.86 per cent. respectively. On drying these samples at 105° to constant weight, which required from four to six hours, water was lost, so that the percentage present after drying was 0.76, 0.51 and 0.55 per cent. respectively. Our results on the green sulphide are in substantial agreement with all other investigators except Muck, who states that 7.43 per cent. of water is present. Other workers find the green sulphide anhydrous or nearly so.

SUMMARY.

Three sulphides of manganese exist, two of which, the red and green, are anhydrous, while the gray sulphide contains a con-

siderable amount of water. The pink sulphide is a mixture in varying proportions of the gray and red sulphides.

The difference in color between the red and green modifications must be due to a difference in molecular structure, the green being probably the more complex. This view is supported by the following facts:

(*a*) The pink or red modification is invariably first formed by precipitation, the green being a transformation product of one of these sulphides.

(*b*) The green modification is more distinctly crystalline and larger-grained.

(*c*) The green sulphide is by far the most stable substance.

Although we have never obtained either sulphide free from sulphur, which can be extracted by carbon disulphide, we do not believe that this sulphur forms part of the molecule of either sulphide, as the properties of neither modification seem to be modified when this sulphur is extracted.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, N. Y.]

DETERMINATION OF MANGANESE AS THE GREEN SULPHIDE.[1]

BY J. C. OLSEN, E. S. CLOWES AND WM. O. WEIDMANN.

Received September 19, 1904.

Two sulphides of manganese have been generally known up to the present time. One of these is pink or flesh colored, while the other is green. These sulphides differ markedly in their physical properties. The pink variety is finely divided, stays suspended in the liquid and passes through the pores of the filter-paper very persistently. The green sulphide is much larger grained, so that it settles readily from the mother-liquor and can be readily filtered and washed.

In quantitative work, therefore, it is very desirable to obtain the green sulphide. As manganese can be weighed with the greatest accuracy as sulphide, this method of determining the element would be much more largely used, if the green modification could be invariably obtained on precipitation. This method of deter-

[1] Read before the New York Section of the American Chemical Society, April 8, 1904.

mination has the advantage over the phosphate method that it separates manganese from the alkaline earth metals, while it is superior to the precipitation of manganese as dioxide in that the latter compound invariably carries down other bases, even the alkalies and, still further, the composition of the ignited oxide is variable.

Practically only two methods for obtaining the green sulphide for quantitative work have been published. The first method was published by F. Muck,[1] in 1869. He obtained the green sulphide by adding ammonium sulphide in excess to a hot solution of the pink sulphide in ammonium oxalate or sulphate. The precipitate first formed was pink, but changed rapidly to green. He states that ammonium chloride in considerable amounts hindered the precipitation and the change from pink to green. If the change did take place, however, the precipitate became very dark and pulverulent. He also states that the green sulphide can not be formed by the use of sodium or potassium sulphide as precipitant.

We repeated his experiments with the ammonium oxalate and found that with a minimum of 0.1 gram of ammonium oxalate for 0.5 gram of manganese chloride the pink sulphide turned green after five minutes' heating. When more of the oxalate was present the change was more rapid. This method could very evidently not be used, if the alkaline earth metals were present, as they would also be precipitated. We have also verified his statements in regard to the influence of ammonium chloride and sodium sulphide. Cleremont and Guiot have also repeated Muck's experiments and obtained the same results.[2]

The second method of obtaining the green sulphide by precipitation has been published by several workers, among whom are Alex. Classen[3] and Fresenius.[4] These investigators recommend to precipitate the manganese from a hot solution, using an excess of ammonium sulphide and to continue heating the solution until the transformation has taken place. A small amount of ammonium chloride must be present to insure complete precipitation of the manganese, but the presence of this salt hinders the conversion of the pink to the green sulphide. The presence of potas-

[1] *Ztschr. Chem.*, 1869, p. 680.
[2] *Bull. Soc. Chim.*, 1877, p. 353.
[3] *Ztschr. anal. Chem.*, **15**, 319.
[4] *J. prakt. Chem.*, **82**, 265.

sium or sodium sulphide also hinders the transformation, and if ammonium sulphide is entirely absent, the pink is not transformed into the green modification. We have tried this method also and have found that in about half of the trials the green sulphide is obtained.

In our experiments a solution of manganese chloride was made of such a strength that 0.55 gram of the salt was present in 5 cc. This amount was used in each case. The volume was always made up to 100 cc. and the precipitations were carried out in Erlenmeyer flasks of 250 cc. capacity. The solutions were heated to the boiling-point before precipitation and if the precipitate did not immediately turn green, the solution was kept almost boiling for one-half hour.

The ammonium sulphide solution was made as follows: Concentrated ammonia was diluted with twice its volume of water. One-half of this solution was completely saturated with hydrogen sulphide, the flask being cooled with tap-water or ice to prevent the formation of the yellow sulphide. The other half of the dilute ammonia was then added. In the preliminary experiments the strength of this solution was assumed to be that calculated from the amount of ammonia present. It was soon suspected that it varied considerably in strength and the following method of titration was adopted: A standard solution of copper sulphate was made by weighing out 15.945 grams of the pure salt and diluting to 1 liter. A measured volume of this solution was warmed and the ammonium sulphide solution added until lead acetate paper was given a brown tinge when held over the nearly boiling solution.

The ammonium chloride solution used contained 265 grams of the dry salt per liter and was, therefore, of five times normal strength.

At first the precipitations were carried out by adding the ammonium sulphide to the boiling hot solution of the manganese and the ammonium chloride made up to 100 cc. In twenty-nine experiments, carried out in this manner, the green sulphide was obtained in only nine cases. In these cases the ammonium sulphide was present in large excess (20 to 37 cc. instead of the 5 to 8.5 cc. necessary for precipitation). The presence of the largest amount, however, did not render its formation certain, an equal

number of pink precipitates being obtained. The presence of even 30 or 40 cc. of 5N ammonium chloride did not seem to prevent the formation of the green sulphide.

The experiments were then repeated with the modification that the manganese solution was poured into the boiling hot solution of the ammonium chloride and sulphide. These experiments were frequently carried out side by side with the preceding experiments so as to secure identical conditions except that of the solution which was poured in. In twenty-eight experiments the green sulphide was always formed when the amount of ammonium sulphide present was from 15 to 64 cc. instead of 2.5 cc., as required for complete precipitation. With smaller amounts of ammonium sulphide a large amount of ammonium chloride prevented the formation of the green sulphide. When the amounts of ammonium sulphide given were present, the presence of even 30 or 40 cc. of 5N ammonium chloride did not prevent the formation of the green sulphide, which, however, was formed more slowly and was of a darker green and more pulverulent.

The method as we have adopted it for quantitative work is as follows: For 150 mg. of manganese 10 cc. of a five times normal solution of ammonium chloride or 2¾ grams of the dry salt and five times the theoretical amount of ammonium sulphide are used. The concentrated solution of the manganese (10 cc.) is *poured into* the boiling hot solution of the ammonium salts (90 cc.) contained in a 250 cc. Erlenmeyer flask. The solution is frequently shaken vigorously and the heating continued until the transformation of the pink (which is always first formed) into the green sulphide is complete. A grayish color is at first noticed, which, on shaking and heating, becomes more and more greenish, until the pink color has entirely disappeared. Failure to secure the transformation has repeatedly been shown to be due to the absence of a sufficient excess of ammonium sulphide.

In order to insure the presence of an excess of ammonium sulphide a number of precautions are absolutely necessary. In the first place the solution must not be boiled for any length of time before the manganese is added, since the ammonium sulphide boils away very rapidly. The reagent must also be prepared immediately before use, as it rapidly turns yellow on standing. Such a solution tends to redissolve the manganese sulphide. 25 cc. of

the ammonium sulphide, prepared as previously directed (page 1624), contains the necessary excess for the precipitation of 0.15 gram of manganese. The precipitate should be digested for about one-half hour. Longer digestion causes the manganese to redissolve because of the formation of the yellow sulphide of ammonium and the volatilization of the excess of the salt. When a large amount of ammonium chloride is present, necessitating long digestion, 40 cc. or more of the ammonium sulphide should be used. After the first half hour's digestion it may be necessary to add 10 or 15 cc. more. The precipitate settles readily, leaving a perfectly clear solution. It is washed with distilled water containing a moderate amount of ammonium sulphide and chloride.

After drying, the precipitate is detached from the paper, which is then burned. The precipitate with the ash is placed in a weighed Rose or porcelain crucible and mixed with two or three times its bulk of sulphur. It is ignited in a stream of dry hydrogen which is free from arsine. A Bunsen burner is used which gives a flame at least six inches high. If the crucible is not heated sufficiently hot, brown manganese dioxide will remain in the precipitate, which should be entirely green. Oxygen or moisture in the hydrogen also tends to form the oxides of manganese. It is cooled in the stream of hydrogen and weighed. We have carried out the entire determination, including the preparation of the ammonium sulphide in about four hours.

In a series of determinations in which 10 cc. of a manganese solution were used the following weights of manganese sulphide were obtained: 0.2248, 0.2248, 0.2244, 0.2248, 0.2246, 0.2248 gram. The average of several determinations of the manganese in 10 cc. portions of the same solution by the Volhard method gave a value corresponding to 0.2243 gram of manganese sulphide, giving a difference between the two methods of 0.4 mg., or about 0.2 per cent. of the weight of the sulphide.

The manganese in another solution was determined[1] by precipitation as the green sulphide. Two 5-gram portions of this solution gave the following weights of manganese: 0.1440, 0.1436, 0.1435, 0.1433, 0.1437, 0.1439, 0.1443, 0.1433 gram. The average of these results is 0.1437 gram. The phosphate determination of the amount of manganese is 25-gram portions of the same solu-

[1] These determinations were made by Mr. W. S. Rapalje.

tion gave the following results: 0.1452, 0.1431, 0.1430, 0.1442, 0.1409, 0.1433 gram. The average of these determinations is 0.1433 gram. The difference between the results by the two methods is 0.4 mg. of manganese. It will be noticed, however, that the maximum difference between the results obtained by the phosphate method is 4.3 mg., while the corresponding difference for the sulphide method is only 0.7 mg.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, NO. 56.]

QUALITATIVE DETECTION OF SACCHARINE IN WINE.

BY ED. MACKAY CHACE.

Received September 28, 1904.

THERE appeared in a recent issue[1] of *La Revue Commerciale et Coloniale,* of Bordeaux, an article by Dr. P. Carles, announcing the discovery of a substance occurring in many French wines which responds to the salicylic acid test for saccharine. In testing for the latter substance by the following method he obtained strong indications of its presence in wines of known purity. Two hundred and fifty cc. of wine were extracted in 50 cc. portions with the same 50 cc. of ether, the ether evaporated and the extracted matter fused wih sodium hydroxide for fifteen minutes. The fused mass was dissolved in water, acidified with sulphuric acid and extracted with low boiling-point gasoline. The gasoline extract was tested for salicylic acid with a dilute solution of ferric alum. In his investigation he used several types of French wines and found the substance in all of them, varying in degree from the red wines to those of the sauterne type, which gave the best reactions.

In order to avoid this substance, which he terms "False saccharine," the same writer, in a later publication,[2] offers a method for testing for saccharine by taste; it is sensitive, however, to but 20 mg. per liter.

It has been known for some time that wines extracted by ether alone would respond to the salicylic acid test for saccharine. C. Schmitt[3] called attention to this fact; he thought the trouble due

[1] December 12, 1903.

[2] Abstract in *Report de Pharm.*, No. 3, 1904, p. 110.

[3] *Report der Anal. Chim.*, 1887, p. 439.

to tannin extracted by the ether and proposed the use of a mixture of low boiling-point gasoline and ether. C. Boucher and F. de Bougne[1] state that this mixture dissolves traces of tannin and that wines thus extracted still give slight tests. They suggest the use of potassium permanganate for oxidizing the tannin, treating the wine before extraction.

M. Ch. Blarez, a friend and co-worker of Dr. Carles, has recently published a method, using the same reagent.[2] He evaporates 300 cc. of wine with 3 grams of syrup of phosphoric acid until free from alcohol, allows to cool and adds in three portions 15 cc. of a 5 per cent. solution of potassium permanganate. After making up to the original volume the liquid is extracted in 100 cc. portions with the same 100 cc. of ether. This method destroys all objectionable substances and, according to the author, is sensitive, testing either by taste or by converting into salicylic acid, to 1 mg. per liter.

In repeating the above work in this laboratory use was made of some seventy-five samples of French sauternes, clarets, German Rhine wines and California wines of the sauterne type. The method used was that described by Carles, except that the extracted matter was heated with sodium hydroxide at 210° to 215° C. for twenty minutes, and that ether was used in place of gasoline for the final extraction. All wines of the sauterne type with one exception gave clear, sharp tests for saccharine. The clarets gave somewhat fainter tests, a few giving none at all. The Rhine wines in most cases gave no test, although some few responded faintly. All the samples had previously been tested in like amounts for salicylic acid with negative results. In many of the wines which gave the heaviest tests for saccharine and which were extracted by the mixture of gasoline and ether, suggested by Schmitt, the salicylic acid was still formed, although the quantity seemed to be somewhat diminished. Another set was extracted with ether after precipitation with basic lead acetate, a treatment which should remove all tannin. The samples thus treated all gave indication of the formation of small amounts of salicylic acid. A few of the above samples, which had given the best tests, were treated with hide powder, thoroughly shaken, and allowed to stand over night, when they were extracted with ether and treated in the

[1] *Bull. Soc. Chim.*, Paris, **29**, 411 (1903).

[2] Abstract in *Report de Pharm.*, **3**, 111 (1904).

usual manner. When tested for saccharine, traces were still indicated. Several tannin extracts and some samples of commercial tannic acid were extracted and tested, a few of the extracts from oak leaves and bark gave very faint tests, but an extract of pecan shells gave a clear unmistakable test. None of the commercial tannic acids responded in the slightest degree.

It would seem, from this test, while some of the salicylic acid formed may be due to tannin, traces are due to some other substances. Further, that all tannins when fused with sodium hydroxide do not yield salicylic acid, for many wines gave no indication of its formation and the wines which yielded the heaviest tests were those containing but small amounts of tannin.

In destroying the substances which interfere with this test for saccharine it is essential to destroy any salicylic acid which may be present, either naturally or added as a preservative. The two methods already mentioned make use of potassium permanganate at normal temperature. At this temperature that reagent in the writer's hands fails not only to destroy small quantities of added salicylic acid, but only imperfectly removes the substances which form salicylic acid on fusion with sodium hydroxide.

After some little experimenting on the effect of a dilute solution of the reagent at boiling temperature upon the saccharine it was found that the following method was very satisfactory: Fifty cc. of the wine were extracted in the usual manner and the extracted matter, after the evaporation of the ether, re-extracted with gasoline. Whether or not the presence of salicylic acid is indicated, this extract is returned to the dish containing the residue from the extraction with gasoline and the whole made up to about 10 cc., 1 cc. of sulphuric acid (1 part in 3) added and the solution brought to boiling. If salicylic acid is present, an excess of a 5 per cent. solution of potassium permanganate is slowly added and the boiling continued for one minute. (If salicylic acid is absent the continued boiling is not necessary.) While the solution is still hot a small piece of caustic soda is added and after standing a few minutes the precipitated iron and manganese are filtered off. The filtrate, which should be strongly alkaline, is transferred to a silver crucible lid, evaporated to dryness and heated to from 210° to 215° C. for twenty minutes. It is then dissolved in a small quantity of water,

acidified with sulphuric acid (1 part in 3) and extracted with ether. The ether extract is tested for salicylic acid with a 0.5 per cent. solution of ferric alum.

This method was tested on all the samples which had responded to the salicylic acid test for saccharine and in no case was that substance formed after the treatment described.

Repeated trials with wine containing added saccharine showed the method to be sensitive to 5 mg. per liter in the absence of added salicylic acid. It destroys the latter substance to the extent of 200 mg. per liter and still detects saccharine present to 10 mg. per liter.

Since offering this paper for publication, the writer's attention has been called to a method by Villiers, *et al.*,[1] in which the material to be tested is first clarified with neutral lead acetate and the excess of lead removed by the addition of a sulphate or phosphate, after which the liquid is extracted with benzene. The benzene extract is tested for salicylic acid. If the taste of this extract leads to the suspicion of the presence of saccharine, it is heated with an excess of potassium permanganate. The fluid is evaporated and heated with 2 cc. of sodium hydroxide in a lead-bath for three minutes to 270° C. It is then dissolved in dilute sulphuric acid and re-extracted with benzene, and the extracted matter tested for salicylic acid. It is the writer's experience that clarification is unnecessary in testing either for saccharine or salicylic acid. In fact, in the presence of only traces of the latter body it is best not to use it. The length of time in which the potassium permanganate is allowed to act upon the extracted matter is not stated in the abstract. Undoubtedly prolonged heating destroys considerable traces of saccharine. Most methods for the conversion of saccharine into salicylic acid limit the temperature to 250° C. The writer's experience is that a somewhat lower temperature is sufficient.

[1] Abstract in *Centralblatt*, 1904, p. 1457.

[CONTRIBUTIONS TO THE CHEMISTRY OF SUGAR ANALYSIS.]

I. POTASSIUM OXALATE AS A LEAD PRECIPITANT IN SUGAR ANALYSIS.

BY HARRIS E. SAWYER.

Received September 29, 1904.

THE official methods of analysis of the Association of Official Agricultural Chemists direct that a solution which is to be tested gravimetrically for reducing sugars shall first be freed of soluble impurities by means of lead subacetate, and that the excess of lead shall then be removed by sodium carbonate previous to the examination with Fehling's solution.[1] Unfortunately, the use of carbonate for this purpose is attended with disadvantages. It was shown some years ago[2] that when lead is removed as carbonate from solutions containing invert sugar or levulose, the use of an excess of alkaline precipitant tends to carry a portion of the precipitate back into solution so that the purpose of the separation is in part defeated. It was proposed, as a remedy for this evil, that the solution be saturated with carbon dioxide after the addition of sodium carbonate; and it was claimed that by this means the lead might be precipitated completely in a granular form well suited to filtration.[3]

The same end may be attained, according to the writer's experience, by substituting sodium bicarbonate for the carbonate. Lead is precipitated quickly and completely, even in the presence of invert sugar, and the precipitate filters well without seeming to redissolve in an excess of the reagent. Unfortunately, however, the use of the bicarbonate has the undesirable effect of converting into carbonate a portion of the sodium hydroxide of the Fehling's solution.

So far as the writer is aware, no exact data have ever been published to show that the addition of a *little* sodium carbonate to a mixture of reducing sugar and Fehling's solution has any effect upon the sugar-copper ratio, so long as the amount of sodium hydroxide in the solution remains constant.[4] Indeed, experiments

[1] Bull. 46; Bureau of Chemistry, U. S. Dept. Agr., p. 33.

[2] Stern and Fränkel: *Ztschr. angew. Chem.*, 1893, p. 579; Bornträger: *Ibid.*, 1894, p. 521.

[3] Stern and Hirsch: *Ibid.*, 1894, p. 116.

[4] Bornträger (*Ztschr. anal. Chem.*, **37**, 160 (1898)) and Bruhns (*Ibid.*, **37**, 244) claim that sugar solutions suffer changes of reducing power when an excess of sodium carbonate is used for the removal of lead, but they refer, presumably, to the use of a *large* excess.

conducted in this laboratory seem to contradict such a view. Thus, to each of four 50 cc. portions of freshly prepared Fehling's solution, 30 cc. of a certain sugar solution were added. To two of these, 20 cc. portions of water were added, bringing the total volumes to 100 cc. To the other two, 20 cc. portions of decinormal sodium carbonate were similarly added. The first two portions gave respectively 0.5155 and 0.5150 gram of cupric oxide; the second two, 0.5151 and 0.5144 gram. The differences between the two sets of results are too slight to be attributed to the influence of the added carbonate.

On the other hand, it is well established that if the amount of sodium hydroxide present in Fehling's solution is varied, the sugar-copper ratio may be affected.[1] It is true that the reducing powers of dextrose and levulose are less influenced by such a variation than those of certain other sugars, and it may be that a reduction in the amount of hydroxide present, through its partial conversion into carbonate, would have less effect upon the sugar-copper ratio than an actual diminution of total alkalinity. But it seems none the less desirable to maintain the proportion of hydroxide as nearly constant as possible, and to avoid the introduction of a bicarbonate or of carbon dioxide in a sugar solution which subsequently is to be tested with Fehling's solution.[2]

On this account it has been attempted to remove the lead in other forms than carbonate. Thus, Gill has recommended its precipitation as sulphite, claiming that an excess of sulphurous acid is without effect on Fehling's solution;[3] and Pellet has employed both sodium sulphite and sulphurous acid, obtaining, however, precipitates which passed readily through filter-paper.[4] Bornträger has studied the use of sodium phosphate as a precipitant, finding that its action is rapid and complete, but that it leaves the filtrate acid and increases the reducing power of the invert sugar contained therein.[5] Many analysts have used sodium sulphate; and Bornträger considers it more generally satisfactory than either the carbonate or phosphate, since the reaction and reducing power of the filtrate remain unchanged.[6]

[1] **Kjeldahl**: "Meddelelser fra Carlsberg Laboratoriet," **4**, pp. 6 and 22 (1895).
[2] **Bruhns**: *Ztschr. anal. Chem.*, **38**, 82 (1899).
[3] *J. Chem. Soc.*, April, 1871, p. 91.
[4] *Bull. de l'Ass'n des Chimistes*, **15**, 524 (1987–'98).
[5] *Ztschr. angew. Chem.*, 1894, p. 521.
[6] *Ibid.*, 1894, pp. 528, 555.

In other respects, however, the sulphate has proved unsatisfactory. The precipitate comes down so slowly as to retard filtration materially, and frequently separates from the filtrate upon the inside of burettes and flasks, making much extra labor in the cleansing of apparatus. These facts have led the writer to the study of another neutral precipitant.

Some years ago the use of ammonium oxalate was suggested by Zamaron;[1] and more recently, Wendeler[2] also recommended precipitating the lead as oxalate, though he insisted that an alkaline oxalate should be employed rather than the ammonium salt. Unfortunately, neither of these writers seems to have given any data regarding the rate or completeness of precipitation, the character of the precipitate, or the action of soluble oxalates on Fehling's solution; and accordingly, the present writer has been obliged to supply these details for himself. He believes that the results about to be reported are not anticipated by any previous publication.

It is desirable, as has already been indicated, that a lead precipitant for use in sugar analysis shall act promptly and completely; that the precipitate shall filter readily, and remain insoluble when an excess of the precipitant is employed; and that the reducing power of the filtrate shall not be altered, either by a change in its reaction or in consequence of the presence of the precipitant. It will be shown that the neutral oxalates of sodium and potassium meet all of these requirements.

EXPERIMENTAL.

Trials have been conducted with both of the above salts, and the two have been found to behave alike; but since the potassium salt is materially more soluble than the sodium compound, it has been given preference. It is now used in the writer's laboratory in the form of a dinormal solution, containing 184.3 grams of the crystallized salt in a liter.

The saccharine lead solution employed in the following experiments was prepared by dissolving 26 grams of cane-molasses in about 500 cc. of water, adding 8 cc. of a solution of basic lead acetate thereto, and filtering after a few moments' shaking. The clear yellow solution thus obtained, containing a considerable

[1] *Bull. de l'Ass'n des Chimistes*, **13**, 346 (1895–'96); **14**, 181 (1896–'97).

[2] *Deutsche Zuckerindustrie*, 1901, p. 1542; Stammer's *Jahresbericht*, **41**, 108 (1901).

amount of lead, will be referred to subsequently as the "sugar-lead" solution.

RAPIDITY AND COMPLETENESS OF PRECIPITATION.

Amount of Precipitant.—To three 80 cc. portions of the sugar-lead solution, labeled A, B and C, were added respectively 1, 2 and 10 cc. of the dinormal potassium oxalate. Each portion was made up to 100 cc. with distilled water, and the mixtures were allowed to stand for about three hours.

In A the lead oxalate precipitate separated slowly, and showed a persistent tendency to pass the filter. Only by using doubled No. 602 S. & S. papers, was it possible to obtain a clear filtrate. Examined under the microscope, the precipitate was seen to consist of granules about 1 μ in diameter, mostly isolated.

In B the precipitate settled more rapidly than in A, and filtered better. Microscopic examination showed that the ultimate particles of the precipitate, still 1 μ in diameter, showed a tendency to form small aggregations.

In C the precipitate settled very rapidly and filtered perfectly. Under the microscope the granules were seen to be gathered into large aggregations.

Portions of all three filtrates were acidified with hydrochloric acid and saturated with hydrogen sulphide. No precipitate or discoloration was observed in any of them, and it was thereby established that the lead had been removed completely, even in A, and that it had not been redissolved by the large excess of precipitant used in C.

The greater ease of filtration displayed by C showed it to be advantageous to use a decided excess of precipitant in case the latter proved to have no effect upon the reducing power of the filtrate.

Rate of Precipitation.—Ten cc. of the potassium oxalate solution were added to about 80 cc. of the sugar-lead solution, and after shaking, three portions were filtered off—respectively, after ten, twenty-five and forty minutes' standing. The perfectly clear filtrates were treated with hydrochloric acid and hydrogen sulphide. In no case was any discoloration to be seen, and it therefore is obvious that precipitation was complete within ten minutes.

EFFECT OF POTASSIUM OXALATE UPON THE SUGAR FILTRATE.

Reaction.—Two 50 cc. portions of the sugar-lead solution were rendered, respectively, very faintly acid and very faintly alkaline toward neutral litmus paper, and to each was added 6 cc. of neutral oxalate solution. When the precipitates had settled, the supernatant liquids were tested again with litmus and were found not to have suffered any change of reaction.

Reducing Power.—The filtrates A, B and C, previously mentioned, were tested for reducing sugars by the gravimetric method, according to Meissl and Hiller. In each case 31 cc. of the sugar filtrate were added to 50 cc. of the freshly mixed copper reagent, the volume was made up to 100 cc. with distilled water, and the mixture boiled for two minutes. Gooch crucibles, loaded with carefully washed asbestos, were used for the filtration, and the precipitate was ignited to constant weight in a muffle, and weighed as cupric oxide. The following weights of oxide were obtained: A, 0.5169 gram; B, 0.5177 gram; C, 0.5177 gram. The one discrepancy is no greater than may occur between duplicate determinations by this method, and the close agreement between the weights of oxide shows that the excess of oxalate was without effect upon the reducing power of the sugar solution.

Further test was made by boiling a mixture of potassium oxalate and freshly prepared Fehling's solution. No reduction was observed.

It may be concluded, therefore, that the neutral oxalate of potassium is a satisfactory precipitant for lead; and since it possesses none of the faults of the carbonate and sulphate, it may advantageously be substituted for them for use in sugar analysis. Did it possess any latent faults, these undoubtedly would have shown themselves in the eighteen months during which it has been employed in the writer's laboratory. So far, the only point noted to its disadvantage is that its solutions show slight growths of mold after long standing. However, no trace of decomposition has been detected as yet, and if such should ever appear, the trouble could, in future, be averted by the additon of an appropriate antiseptic.

FROM THE LABORATORY OF FELTON AND SON,
BOSTON, MASS.

THE TECHNICAL ANALYSIS OF CEMENTS.

By S. F. Peckham.

Received October 1, 1904.

The recent publication of the paper, by Mr. Bertram Blount, on "The Analysis of Portland Cement,"[1] again brings to the attention of chemists this important question that had been allowed to slumber for some months.

The very satisfactory results and conclusions reached by Mr. Blount, with which I almost wholly agree, led me to a reperusal of the papers read by Dr. Hillebrand, and to a reconsideration of the subject. The practical value of the conclusions reached by Mr. Blount cannot be overestimated, and I say this without any intention of underestimating the intrinsic value of all the work done by Dr. Hillebrand,[2] and Mr. Richardson's committee. Whether or no it is desirable to formulate a process of analysis that all chemists may be expected to follow, the indirect results that have followed the work of this committee and the discussion that has proceeded from it, have proved to be of such value as to wholly justify all that has been done by all the parties concerned.

I think, however, that in the presentation up to this date, several very important aspects of the general subject have been lost sight of or overlooked. The discussion has proceeded as if there was little or no variation in the quality of cements, also as if there was one invariable purpose in the analysis of cements, and further, the analysis of the slurry and other substances used in the manufacture of cement has been mixed up with the analysis of cements, as if the sole object of the committee had been to devise the best scheme for the analysis of a uniform material for a uniform purpose.

Now I think it is quite clear that the problems presented to a chemist in a cement manufactory, and the problems presented in a city laboratory, and the problems presented to Dr. Hillebrand, are wholly different and require for their solution consideration of wholly different methods of procedure. The problems presented to Dr. Hillebrand were wholly scientific and have been treated by him in a manner that leaves nothing to be desired. If

[1] This Journal, **26**, 995.

[2] *Ibid.*, **25**, 1180.

I understood him correctly, in a conversation, he said that the technical aspects of the subject had not been presented to him and had not been considered by him. Such a conclusion is to be reached from a perusal of his papers. A further conclusion is to be reached by their perusal, *viz.*, that such methods of manipulation as he recommends, intrinsically valuable as they are, can be used to very little purpose by the class of manipulators that he describes.

It is to be presumed that a majority of these men who work with dirty water and impure reagents have passed scores of examinations successfully, and have worked up with the aid of their intructors, a thesis for a doctor's degree, cramming themselves full of information about things without the slightest appreciation of the temperamental and psychological qualities essential to the solution of chemical problems. I once remarked to a young professor of chemistry that a successful chemist must be a creator. He stared at me in open-eyed wonder and asked me where I could find one. What more striking demonstration could be found of the truth of Sir William Ramsay's strictures on technical education, that present methods develop memory and leave the inventive faculties dormant; that they show only what a man knows and not at all what he can do.

To return to our subject, it seems to me that while the strictly scientific aspects of the subject have been discussed in a masterly and well-nigh exhaustive manner, resulting in the presentation of a large amount of analytical data of the greatest value, the questions have been left wholly undetermined whether or no ultimate methods of analysis are to be applied indiscriminately to the solution of the three classes of problems mentioned above; or, if proximate methods are preferable, in what cases are they preferable?

Those engaged in the manufacture of cement can best decide what method of analysis will best solve the problems presented to them.

So, too, those who use cement and those who control the use of cement can best decide what methods are best suited to the time, place, conditions and identity of the problems presented to them for solution. For illustration: In a laboratory where determinations of lime are of daily occurrence, the use of permanganate

solution may be both convenient and expeditious; but in a laboratory where the work is very varied and the aggregate of lime determinations does not occupy more than six weeks in a year, more time is lost in adjusting the permanganate solution than is saved by its use. There are a multitude of reasons, too numerous to mention, why the judgment of Mr. Blount is sound, that each chemist should be left free to decide for himself what analytical methods he will use, for if the analyst is not capable of making this decision, he is like a general in the field, subject to the dictation of a bureau.

Instead of having a number of uniform problems presented to this laboratory relating to cements, scarcely two of them have been exactly alike. To treat them uniformly by the most elaborate method of ultimate analysis, even as faultlessly arranged as that of Dr. Hillebrand, with determinations of titanium and phosphates, carried to a thousandth of a per cent., and with silica twice evaporated, and all the other refinements, would be a waste of time to little or no purpose. First-class cements containing a minimum of insoluble matter are rarely brought to this laboratory. The first determination I make is for "matter volatile at a red heat." For this purpose we, some time ago, installed an electrical muffle that with a current of given intensity, controlled by a rheostat, gives a uniform low red heat. Using two half-ounce platinum crucibles, duplicate determinations can be made with great accuracy.

I then weigh out 5 grams of the cement, just as it is received. To dry or pulverize it would make another and different sample of it. I use 5 grams instead of 0.5 gram for the reason that I have found, by considerable experience with students, that the number of human beings who are endowed by nature with the capacity to manipulate successfully and accurately very minute quantities, is, as a rule, very small. If 5 grams are taken, on an average there will be left enough insoluble residue for examination by fusion, if desired. True, there is more silica dissolved on an average than is necessary; but, generally, when a reasonably large amount is taken, the errors are compensated by a smaller proportional personal equation and smaller loss. All of the *cement* is decomposed by 10 per cent. hydrochloric acid. If the solution is made slowly and with care, no soluble silica is rendered in-

soluble, hence there is no need of the use of sodium carbonate. No process for the manufacture of cement is practically perfect, hence a small percentage of overburned or underburned slurry is to be expected in an average sample of even the best cement, along with an always present percentage of the ash of the coal that is blown into the rotary kiln. None of this material is cement and no method of analysis should be used, such as the use of strong acid that will decompose the ash, or of sodium carbonate that may dissolve part of the silica that is not in combination as cement, and thereby increase the percentage of silica apparently present as a constituent of the cement. While in this particular I do not agree with Mr. Blount, I do not question his conclusions concerning coarse cements that dissolve slowly. The solution cannot be hurried. A great deal of work has been done in this laboratory upon several hundred samples of cements of very differing quality. In no case, that has been tested, has any lime been found in the residue from 10 per cent. hydrochloric acid. An attempt was made to secure an acid that would decompose calcium carbonate and leave the cement intact, but wholly without success. Organic acids that were strong enough to decompose carbonates invariably decomposed the cement and sometimes rendered the silica insoluble.

Applied to several hundred problems, now for several years, the method that I recommend for bringing the silica that forms a part of the cement into solution, has been found to be wholly satisfactory for technical purposes. I, therefore, insist that it is neither "puzzolanic material" nor ashes that should be decomposed, but cement. When Mr. Blount admits that by the use of either supplementary grinding or strong acid, other silica than that constituting cement is brought into solution along with that contained in the cement, he yields all that for which I have been so long contending and which Dr. Hillebrand recommends. I evaporate the silica solution over night over a water-bath heated by an electrical stove. Morning usually finds the residue dry at a temperature below the boiling-point of water. Heating to a temperature of about 250° F., on an electrical stove, completes the dehydration at a uniform and low temperature. I am not prepared to say that small quantities of silica do not remain in solu-

tion on a single evaporation, but for technical purposes it is a negligible proportion of that contained in 5 grams.

The filtrate from the silica is made up to a liter and two portions, of 100 cc. each, are measured into two Becher glasses. The average technical analyst has no time to redistil ammonium hydroxide. It is much more economical of time to assume a contamination with ammonium carbonate and reprecipitate. This is not a long operation, especially with a filter pump, and is *always* safe. For technical purposes the lime and magnesia are easily determined with one precipitation each, although each may be contaminated with a trace of the other.

It is rare that for technical purposes a determination of carbon dioxide or alkalies is necessary.

While thanking Dr. Hillebrand and Mr. Blount for all the good things they have said and done, I am confident that the scheme above set forth will be found to furnish all the information necessary for the solution of a great number of technical problems, for which the elaborate niceties of Dr. Hillebrand's scheme were never intended, and for which they should never be recommended.

LABORATORY OF THE COMMISSIONERS OF ACCOUNTS,
NEW YORK, September 30, 1904.

[CONTRIBUTION FROM THE UNIVERSITY OF ILLINOIS AGRICULTURAL EXPERIMENT STATION No. 12.]

THE DETERMINATION OF ORGANIC CARBON IN SOILS.

BY J. H. PETTIT AND I. O. SCHAUB.

Received September 16, 1904.

IN CONNECTION with the chemical side of the soil investigations now being carried on at this Station, it was desirable to know the organic carbon content of a large number of soils. The copper oxide combustion method was too long and tedious, and the wet combustion method, using potassium dichromate and concentrated sulphuric acid, did not give complete combustion on chemically pure organic compounds like sugar. Accordingly, Parr's[1] method for carbon in coal was tried for soils. After some modifications this method gave results which compare very favorably with the copper oxide combustion method, and it has the advantage of being much more rapid than other methods used.

[1] This Journal, **26**, 294.

Four determinations on chemically pure sugar gave the following results by this method:

Weight taken. mg.	Weight carbon. Calculated. mg.	Weight carbon. Found.[1] mg.	Carbon recovered. Per cent.
150	63.15	62.81	99.46
150	63.15	62.85	99.52
150	63.15	63.08	99.89
150	63.15	62.84	99.51

The percentage of organic carbon in most soils is low, and it is usually necessary to add some easily combustible material to the charge in order to start the combustion.

Sulphur used for this purpose, as suggested by Professor Parr, gave sulphur dioxide in the gas resulting from the treatment of the charge with acid after the combustion in the bomb, and this was not prevented by the use of potassium nitrate in the charge. Powdered magnesium was then tried in place of the sulphur. One gram of finely ground magnesium powder, thoroughly mixed with a charge of 2 grams of soil and 10 grams of sodium peroxide, gave a complete and satisfactory combustion with all soils ranging from 0.1 per cent. to 3.5 per cent. organic carbon.

The magnesium is not always completely oxidized, however, and that which remains as metallic magnesium will, of course, liberate hydrogen when the charge is treated with acid to set free the carbon dioxide. To avoid error in this way the gas, after measuring, is forced into a Hempel pipette filled with potassium hydroxide (2:1) and the carbon dioxide absorbed, the residue being drawn back into the burette and a second reading taken. The time taken for this absorption and extra reading is compensated by time saved in the previous manipulation by not having to measure out exactly 100 cc. of air. A determination of the inorganic carbon is made in the same apparatus by treating a sample of the original soil with acid and measuring the liberated carbon dioxide. The total carbon found by the combustion less the inorganic carbon gives the organic carbon.

The soils used represent types ranging from a poor silt, low in organic matter, to a drained swamp soil, high in organic matter. The first sample in each set of three is the plowed soil taken to a depth of seven inches. The second sample is the soil between the

[1] Computed from volume of carbon dioxide measured at known temperature and pressure.

plow line (seven inches) and the subsoil line (usually about eighteen inches); and the third is a sample of the subsoil to a total depth of forty inches.

The method was checked up with the copper oxide combustion method and the following table gives some comparative results:

PER CENT. ORGANIC CARBON IN SOILS.

Soil No.	Soil stratum.	Copper oxide method.	Parr's method modified.	Difference.
59	Surface	3.39	3.40	+ 0.01
60	Subsurface	2.08	2.11	+ 0.03
61	Subsoil	0.45	0.54	+ 0.09
89	Surface	3.32	3.35	+ 0.03
90	Subsurface	1.92	1.98	+ 0.06
91	Subsoil	0.54	0.67	+ 0.13
119	Surface	3.15	3.15	+ 0.00
120	Subsurface	2.36	2.42	+ 0.06
121	Subsoil	0.65	0.74	+ 0.09
473	Surface	0.87	0.94	+ 0.07
474	Subsurface	0.36	0.39	+ 0.03
475	Subsoil	0.12	0.13	+ 0.01
556	Surface	8.37	8.38	+ 0.01
557	Subsurface	1.48	1.64	+ 0.16
558	Subsoil	0.22	0.24	+ 0.02
661	Surface	3.93	3.96	+ 0.03
662	Subsurface	2.45	2.48	+ 0.03
663	Subsoil	0.48	0.43	— 0.05
690	Surface	1.29	1.39	+ 0.10
691	Subsurface	0.61	0.59	— 0.02
692	Subsoil	0.44	0.36	— 0.08

With this method, using Parr's apparatus, one man can easily make duplicate determinations on eight soils in a day of eight hours. One man has made nineteen separate determinations in one day in this laboratory.

INACTIVE THORIUM.[1]

BY CHAS. BASKERVILLE AND FRITZ ZERBAN.

Received October 19, 1904.

Synopsis.—A new source of Inactive Thorium has been found in a rock from South America.

Most of the investigators working on radio-activity are of the opinion that thorium is a primarily active body, under all condi-

[1] Read before the New York Section of the American Chemical Society and published by permission of the Carnegie Institution.

tions, independently of the source from which it is obtained. K. A. Hofmann, and also the writers, arrived at the assumption that thorium is inactive *per se* and shows radio-active properties merely under certain circumstances.

One of us investigated Rutherford's thorium-X, especially for its chemical properties.[1] Through the courtesy of the Welsbach Lighting Company he obtained over 100 liters of an ammoniacal filtrate by the extraction of thoria from monazite sand, which is said to contain thorium-X. This liquid, after evaporation and ignition, left a residue showing strong radio-activity, but no trace of thorium could be detected in it. Further, by reprecipitation of a quite chemically pure thorium solution with fumaric acid, according to Metzger's method,[2] evaporation of the filtrate and ignition, a residue was obtained much more active than the precipitate. These two results can be explained only by the fact that the radio-activity of the common pure thorium preparations is not a property of thorium itself, but of a strange body associated with it.

Now, while it has been found impossible as yet to remove this additional substance thoroughly from thorium, K. A. Hofmann and Zerban did succeed in obtaining entirely inactive thorium directly from mineral sources,[3] but only from such minerals as contain no radio-active bodies at all; for instance, from Norwegian gadolinite, yttrotitanite and orthite. On the other hand, it has been found that thorium is active only when, but always when the minerals yielding it contain other radio-active substances.

In these investigations it was, also, necessary to state the presence of other radio-active bodies than thorium in monazite sand, which was said to contain only thorium as a radio-active body. Indeed, one of us detected very small amounts of uranium in five different samples of monazite sand from various localities.[4] Some time ago Clemens Winkler made some objections to the method used in this work.[5] This matter will be taken up later.

Clemens Winkler also suggested that there are uranium-free monazites, but, in the meantime, Haitinger and Peters have noted

[1] This Journal, **26**, 922 (1904).
[2] *Ibid.*, **24**, 901 (1902).
[3] *Ber. d. chem. Ges.*, **36**, 3093 (1903).
[4] *Ibid.*, **36**, 3911 (1903).
[5] *Ibid.*, **37**, 1655 (1904).

the presence of radium in monazite sand. So the radio-activity of thorium from uranium-free minerals may be explained by the presence of radium in them.

In continuing the work on the activity of thorium we analyzed a mineral, or more properly speaking, a rock, from South America which yielded perfectly and initially inactive thorium. This rock possesses a grayish color, very similar to common slate.[1] It consists mostly of barium carbonate, containing a very small percentage of thoria.

Neither the barium nor the thorium in this rock shows any radio-activity. There are no α-radiations given off, and barium within 140, thorium within 290 hours did not affect the photographic plate through black paper.[2] That our body is really thorium could be proved by the different reactions characteristic for this body: As, first, solubility of the oxalate in a hot solution of ammonium oxalate and reprecipitation of the oxalate after diluting and cooling; second, by precipitation with sodium thiosulphate, potassium iodate, fumaric acid, *m*-nitrobenzoic acid, and phenylhydrazine. The quantity of the body obtained was very small, so that we could not carry out a determination of the atomic weight. We are now occupied, however, in working with larger quantities of the rock and hope to be able soon to determine whether or not this new variety of thorium is of a simple elementary nature or capable of being resolved into the three constituents, berzelium, carolinium, and new thorium.

The important bearing these observations have on the very recent theories of radio-activity is apparent.

CONTRIBUTION FROM THE COMMITTEE ON UNIFORMITY IN TECHNICAL ANALYSIS, I.

Received October 24, 1904.

THE object of the present communication is to offer to American chemists a sketch of the reasons for the existence of the Committee on Uniformity in Technical Analysis and a statement of the policy by which it expects to be guided in seeking to remedy the present very unsatisfactory condition of analytical chemistry in at least some lines of work.

[1] We are indebted to Dr. Geo. C. Lee, of Philadelphia, for the material.

[2] Even after an exposure of 600 hours no effect upon the plate can be noted, as two subsequent experiments show.

The causes to which the committee owes its existence can best be made clear by a review of the work done by several committees in the lines of cement, copper slag and zinc ore analysis, with the coöperation of a large number of chemists throughout the country.

REVIEW OF PAST WORK.

In 1901, Mr. Clifford Richardson presented before the New York Section of the Society of Chemical Industry an address in which he showed the lamentable lack of agreement among different chemists in analyzing Portland cement. The result of his recommendations was the appointment of a committee of the Section to consider the subject of technical analysis, the first line of work taken up practically being that of the analysis of Portland cement and raw cement mixtures, by a subcommittee consisting of Messrs. Richardson, S. B. Newberry and H. A. Schaffer. The results of their labors have been made public in the *Journal of the Society of Chemical Industry*, **21**, 12 and this Journal, **25**, 1180. Discussions of and criticisms upon these reports have appeared at one time and another, notably in the *Journal of the Society of Chemical Industry*, **21**, 830 and 1216, and this Journal, **26**, 995; also *Cement and Engineering News*, **16**, 37. Opinions differ as to the merits of the proposed analytical procedures, but the general effect of the sub-committee's work has been to greatly stimulate interest in the matter of cement analysis by the bad showing made, and to create a desire for greater uniformity in results. Owing to the wide publicity given to these reports, they will not be here discussed, though the extreme results rendered by the coöperating analysts will be reproduced farther on.

Inspired by his own experience, Mr. Thorn Smith, of Isabella Tennessee, had undertaken, independently of Mr. Richardson's committee and without knowledge of its operations, to ascertain the actual state of analysis with respect to copper slags, by enlisting the coöperation of a large number of chemists in the analysis of a sample prepared and distributed by himself. The results of this work were later placed in the hands of Mr. Richardson's general committee, and, as in the case of the cement analyses, a critical report was rendered at their request by Dr. Hillebrand, of the United States Geological Survey. This report has never

been published, though copies were placed in the hands of the chemists who had furnished analyses. The original analytical returns with comments by Mr. Thorn Smith, based on Dr. Hillebrand's report, appeared in the *Engineering and Mining Journal*, 75, 295, to which reference should be made for details. Certain data from this report will follow those relating to cements farther on.

Later, a sub-committee on zinc ore analysis was appointed, consisting of Mr. W. George Waring, of Webb City, Mo., and Mr. George C. Stone, of New York City. They distributed three samples of ore differing widely in character, and received more or less complete returns from forty-two chemists, on the basis of which the sub-committee has prepared a valuable report, which will receive attention in its proper place.

Meanwhile, for reasons which are not pertinent to this report, the central committee of the New York Section of the Society of Chemical Industry was dissolved, and the laudable aims which it sought to attain might have failed altogether of further pursuit had not the Council of the American Chemical Society directed the appointment of the present committee for the purpose of continuing the work begun by its predecessor in the other Society. The report on zinc ore analysis, above alluded to, is now in the hands of our committee, and Messrs. Waring and Stone will be continued as one of its sub-committees for the purpose of accumulating further data of an important character upon which to report at a later date.

In the first three of the following tables are presented briefly, for convenient reference, the extreme results reported by the chemists who coöperated with the former sub-committee on cement analysis and with Mr. Thorn Smith. They are followed by a detailed table of results reported by the zinc ore sub-committee and an abstract of certain features of that report. Greater space is devoted to this than to the other reports for the reason that it has not appeared in print and it is desirable that those who are engaged in the work of analysis be put in possession of the results of their fellows without further delay.

TABLE I.—EXTREME RESULTS ON (*a*) ORIGINAL CEMENT RAW-MIXTURE, (*b*) ORIGINAL FINISHED CEMENT.

		SiO_2.	$\frac{Al_2O_3}{Fe_2O_3}$.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SO_3.	Ign.
(*a*)	High	15.75	8.50	6.64	2.73	41.92	2.14	....	....
	Low	12.78	7.08	5.27	1.26	39.53	1.10	....	....
(*b*)	High	21.56	11.36	8.20	3.76	64.30	3.15	1.71	3.20
	Low	19.18	9.32	6.26	2.30	62.01	2.52	1.30	1.04

TABLE II.—EXTREME RESULTS ON SECOND SAMPLE OF (*a*) RAW MIXTURE, (*b*) CEMENT.

		SiO_2.	$\frac{Al_2O_3}{Fe_2O_3}$.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SO_3.	Ign.
(*a*)	High	15.54	7.07	4.13	2.66	42.27	1.50	1.75	39.68
	Low	12.10	4.20	2.36	1.14	40.21	0.62	1.42	35.15
(*b*)	High	22.86	9.68	6.46	4.30	64.43	2.82	2.26	4.50
	Low	20.50	8.36	4.88	2.26	62.14	0.95	1.38	0.98

It may be said with regard to the results of Table II that it was intended they should be arrived at according to a method suggested by the sub-committee on cement analysis, but they are in no way to be taken as a fair test of that method, for the reason that its provisions were adhered to by so few of the analysts. Nevertheless, notwithstanding the wide variations between extremes, a critical review of all the data showed that marked progress had been made in certain directions.

TABLE III.—EXTREMES ON COPPER SLAG BY NINETEEN ANALYSTS.

	SiO_2.	Fe.	Al_2O_3.	CaO.	MgO.	Zn.	Mn.	Cu.	S.
High	35.15	32.20	7.16	13.53	3.21	4.25	1.53	0.46	1.98
Low	31.27	30.33	3.24	10.73	1.20	1.87	0.11	0.20	1.45

It may be added for these figures that they do not tell the whole truth. Only those have been included which it seemed worth while to consider in a general discussion of the causes of variation. Certain values, reported by one or two analysts, were omitted as not entitled to consideration, though included in the originally published tables.

DATA FROM UNPUBLISHED REPORT OF SUB-COMMITTEE ON ZINC ORE ANALYSIS.

TABLE IV.—ASSAYS OF ZINC ORES BY FORTY-TWO CHEMISTS.

	Sample A.[1]			Sample B.[1]			Sample C.[1]		
	Zn.	Method.	Fe.	Zn.	Method.	Fe.	Zn.	Method.	Fe.
1	59.06	3	2.28	17.96	3	20.63	31.47	3	11.06
2	58.64	7	2.38	17.42	7	19.99	31.97	7	10.74
	58.90	3	...	17.59	3	....	32.08	3	....
	59.73	3	...	18.21	3	....	32.50	3	....
3	57.10	3	2.96	17.70	3	20.52	28.90	3	10.40
4	57.65	3	2.61	18.81	3	20.76	32.81	3	....
5	57.83	3	2.67	18.10	3	20.92	32.13	3	10.92
6	57.52	4	2.86	38.15	4	18.04	38.77	4	11.02
7	59.13	4	...	39.22	4	....	37.05	4	....
8	58.37	4	2.30	18.90	6	18.80	31.30	5	10.60
9	58.47	4	2.80	18.65	6	19.50	31.39	5	10.90
10	57.90	1	2.10	13.00	1	19.90	30.90	1	15.00
11	58.40	4	2.40	18.40	6	20.60	31.80	5	11.00
12	57.80	7	3.26	17.80	7	21.42	31.00	7	12.51
	57.80	7	3.26	17.95	7	21.80	31.10	7	12.90
13	58.30	4	...	12.85	1	....	31.30	1	....
	58.35	4	...	16.90	6	....	31.80	5	....
	58.35	4	...	16.90	6	...	31.90	5	....
	....		...	17.80	8	....	32.80	5	....
	....		...	17.90	6	....	33.00	5	....
	....		...	18.20	7	....	33.20	5	....
14	58.30	4	...	17.90	6	....	33.00	5	....
15	58.30	1	...	12.87	1	....	31.60	1	....
	....		...	17.80	6	....	....		....
16	58.30	4	2.20	17.30	6	19.64	31.60	5	10.04
17	58.65	2	2.42	17.20	2	21.20	30.85	2	10.44
18	....		...	12.98	1	....	30.54	1	....
19	58.41	1	2.42	18.74	2	20.34	31.62	1	10.80
20	58.78	4	2.72	19.42	6	21.13	31.65	5	11.08
21	58.42	1	...	15.21		21.05	30.83	1	....
	....		...	16.23	7	21.92	....		....
22	58.35	4	2.64	16.94	6	20.40	31.25	5	10.29
23	56.03		2.30	15.60		19.55	30.28		10.60

[1] A. Blende from Joplin, Mo.

B. Oxidized ore from New Jersey, containing franklinite, willemite and zinc spinels.

C. Impure blende from Colorado.

Mr. Waring analyzed the ores and his results for the important constituents follow, those for zinc being the average by three methods, those for cadmium the mean of duplicate determinations.

	A.	B.	C.
Zn	58.25	18.16	31.48
Fe	2.38	20.36	10.77
Mn	....	9.37	....
Cd	0.34	....	0.016
Cu	0.08	....	6.92
Pb	1.82	....	13.80

	Sample A.			Sample B.			Sample C.		
	Zn.	Method	Fe.	Zn.	Method.	Fe	Zn.	Method.	Fe.
24	59.79	4	3.23	17.60	6	20.75	30.77	5	13.03
	....		...	32.14	4	....	....		....
25	57.73	1	2.70	19.57	2	20.59	33.83	1	11.33
26	38.23	1	2.51	17.53	2	20.58	31.08	1	10.80
27	57.30	1	...	12.50	1	....	30.80	1	....
28	58.00	1	...	....		....	....		....
	58.00	1	...	....		....	....		....
29	58.50	4	2.50	13.00	1	20.80	32.40	5	8.40
30	50.80	1	2.50	12.53	1	20.05	31.40	1	11.45
	....		...	17.83	8	....	....		....
	. ..		...	18.11	6	....	....		. ..
31	57.73	7	...	18.24	7	....	32.41	7	....
	58.37	1	...	18.33	7	....	32.51	7	....
32	58.90	1	2.30	12.60	1	20.20	30.20	1	11.30
33	58.10	8	2.38	12.20	1	20.35	30.90	5	10.77
	58.25	4	...	12.73	1	....	31.28	8	....
	58.40	8	...	13.74	1	....	31.38	7	....
	58.40	4	...	17.53	2	....	....		....
	58.59	8	...	17.87	2	....	31.45	8	....
	....		...	....		....	31.51	8	....
	....		...	17.89	7	....	31.60	5	....
	....		...	17.95	6	....	....		....
	....		...	17.98	8	....	....		....
	....		...	18.09	8	....	....		....
	....		...	18.10	2	....	....		....
	....		...	18.15	8	....	....		....
	....		...	18.15	2	....	....		....
	....		...	18.24	7	....	....		....
	....		...	35.12	4	....	....		....
34	57.85	4	2.40	....		....	31.10	1	8.60
35	58.10	4	2.30	22.76	6	20.60	31.90	5	8.80
36	55.97	3	...	17.85	3	....	38.86	3	....
37	57.58	1	...	14.35	1	....	30.96	1	....
	58.47	7	...	18.21	7	....	31.53	7	....
38	58.03	4	2.77	17.99	7	20.14	31.09	7	11.47
39	59.72	3	2.38	18.22	3	19.89	32.54	3	10.74
40	57.50	4	2.40	23.30	6	20.29	30.90	5	10.71
41	57.85	3	...	....		....	....		....
42	59.12	1	...	14.73	1	....	31.16	1	....
High	59.73		3.26	39.22		21.92	38.86		15.00
Low	56.03		2.10	12.20		18.04	28.90		8.40

Of the forty-two chemists whose returns are listed above, "twenty-three are, or were, in zinc works, three in other works where zinc is frequently determined, eleven were commercial chem-

ists, most of whom make a specialty of zinc, and five were professors or instructors in colleges. The samples were sent to a number of other college men, all of whom either declined to analyze them or failed to report after repeated requests to do so."

After a brief discussion of the figures for iron, the authors say: "It is certainly not to the credit of the analysts that such enormous differences should exist in as simple a determination as iron," a conclusion which is fully in accord with those expressed by Dr. Hillebrand in his reports on the cement and copper slag analyses.

Naturally, the greater part of the report is devoted to the zinc figures. The methods used for determining zinc were numerous and are numbered in the table.

1.—Low's method (*Proc. Colo. Sci. Soc.*, **4**, 179; this Journal, **22**, 198).

2.—Hinman's modification of 1, using hydrochloric acid as the solvent (*School of Mines Quart.*, **14**, 40; Furman's "Assaying," 4th ed., p. 207).

3.—Wintersteen's method, unpublished, but practically the same as Voigt's (*Ztschr. angew. Chem.*, 1889, p. 307), using citric acid for tartaric acid.

4.—The Joplin method, which is practically the Fahlberg method (*Ztschr. anal. Chem.*, **13**, 379, and Waring in this Journal, **26**, 20-22).

5.—This is 4, modified so as to remove copper by lead, or lead, copper and cadmium by aluminum or hydrogen sulphide (this Journal, **26**, 23-24).

6.—Methods in which the iron is removed by ammonia, barium carbonate or as basic acetate, and the manganese by an oxidizing agent. The zinc usually titrated, but in some cases weighed. Copper in all cases removed (this Journal, **26**, 23-24).

7.—Methods in which copper was separated, the iron precipitated as in 6, and the zinc by hydrogen sulphide from an acetic solution and then either weighed or titrated (Mahon: *Am. Chem. J.*, **4**, 53).

8.—Waring's method (this Journal, **26**, 26-27).

Upon tabulating the results for each sample separately by methods, the authors were able to discuss the data intelligently

and to draw certain conclusions, which will not now be reproduced, but reserved for a later report, after additional data have been accumulated with respect to method No. 8. The most superficial examination of these tables, which those interested can construct for themselves from the data of Table IV, will make it obvious that some of the methods in common use are not by any means of universal application.

COMMENTS.

The showing of the Tables I to IV is ample demonstration that analytical chemistry, as ordinarily practiced, is anything but an exact branch of the chemical profession. Mr. Waring has furnished additional data from his own experience, to which nearly every chemist could add, showing the lack of agreement that is all too common, often leading to serious consequences, aside from the reflection cast upon the profession at large.

That this is a state of affairs not only of long standing, but long since discovered in certain lines of work, is sufficiently attested by the addresses, first of Dr. C. B. Dudley on the subjects of discrepancy in analysis, and standard methods for the analysis of iron and steel,[1] and secondly of Baron Hans Jüptner von Jonstorff.[2] Most of the causes underlying variations in results of different chemists have been very fully discussed by these gentlemen, and a perusal or reperusal of their papers and the discussions following them will be time well spent by most analysts. To repeat the substance of them here would lead too far. Suffice it to say that sources of error were pointed out besides the familiar ones of lack of uniformity in samples, poor quality of reagents, etc., or defects in the method or the chemist himself, such as the employment of different atomic weights. This last, while not a prolific source of error, may, as pointed out by Baron Jüptner, give rise at times to serious mistakes. That due to poor reagents will, in time, it is hoped, be lessened as a result of the work now being done by a committee of this Society, in coöperation with the National Bureau of Standards.

With samples of the kind represented by the analyses of Tables I to III, marked errors due to mechanical sorting of once homo-

[1] *Eng. Soc. Western Penna.*, September, 1892, and October, 1893; this Journal, **15**, 501 (1893).

[2] *J. Iron and Steel Inst.*, **49**, 80 (1896).

geneous materials must, from the very nature of those materials, be out of the question. Even with the zinc ores of Table IV the errors are of such a character as to render non-homogeneity, as well as most of the other ordinarily enumerated causes of error, quite inadequate as an explanation. There is a growing and seemingly well-grounded opinion, which has been given expression by Mr. Thorn Smith and the authors of the zinc report that our methods of teaching are largely accountable for the unsatisfactory state of affairs. There is abundant evidence in the mass of data accumulated by the several sub-committees referred to in support of this view, after making full allowance for the fact that with the best instruction not all students will make good chemists.

POLICY OF THE COMMITTEE.

In view of the facts set forth, this committee has adopted the following policy for the guidance of its work, a policy which is subject to change or expansion, as the need arises.

(1) To use every endeavor to impress upon chemists the necessity for such changes, either in methods of analysis or of manipulation, together with a control of the purity of reagents in use, as will make it possible to arrive at greater uniformity in the results of analyses made by different analysts.

(2) To determine whether the lack of uniformity is to be attributed to lack of proper instruction in our schools or to mere carelessness in manipulation, by inviting the coöperation of the instructors in analytical chemistry in the work, distributing among them standard material for analysis, the results of the analysis of which shall demonstrate the accuracy of the method taught by them.

(3) To test, in conjunction with the National Bureau of Standards, various methods, and determine their accuracy and suitability for general use.

It may be said in this connection that the hearty coöperation of the Bureau of Standards has been promised, contingent only on the appropriation by Congress of the funds needed to secure the help of competent chemists. Application for such an appropriation will be made at the coming session of Congress, and it is the desire of the Committee that friends of this movement use what influence they may possess to forward it. This may be

done, in part, by presenting in writing to the Director of the Bureau arguments in favor of coöperation, especially when strengthened by a clear statement of specific problems whose settlement may have commercial importance.

(4) To prepare samples of materials of different character whose exact composition shall have been determined by the most careful analyses of experts.

(5) To place such samples in the care of the National Bureau of Standards for preservation and distribution to persons desiring to test their methods of analysis or of manipulation, or to check the work of students or technical chemists employed in works.

(6) To invite the coöperation of persons interested in the analysis of any particular class of material, by the organization of sub-committees for the preparation and distribution of samples, the chairman of which shall be, for the time being, a member of the general committee and entitled to vote on the subject which his sub-committee has under consideration.

It will not be the policy of this Committee to commit the Society as a body to the endorsement of any methods as standard, but merely to recommend such as may be found satisfactory. Nor will the Committee intrude on fields of work that may be already well covered by existing organizations, such as the Society of Official Agricultural Chemists.

Suggestions as to modifications of the policy of the Committee, or criticisms of it, will be thankfully received.

W. F. HILLEBRAND, *Chairman*,
CHAS. B. DUDLEY,
H. N. STOKES,
CLIFFORD RICHARDSON, *Secretary*.

NEW BOOKS.

THE INDUSTRIAL AND ARTISTIC TECHNOLOGY OF PAINT AND VARNISH. By ALVAH HORTON SABIN, Chemist for Edward Smith & Co. New York: John Wiley & Sons. First edition. 1904. Octavo. vi + 372 pp. Price, $3.00.

Prof. Sabin has brought together widely scattered notes and references to the early history of the linseed oil and varnish industry, which are not accessible to the general reader, together

with his own experience in the methods used in the manufacture of varnish and paint at the present time.

The book is of much interest to those desiring general information on the principles of varnish-making, treatment of linseed oil, protection of metal surfaces against corrosion, result of exposure tests of different coatings in salt and fresh water, and similar questions.

The chapter on Chinese and Japanese lacquers probably gives the most reliable data on this little-known subject. The compilation of early references to paint and varnish shows a very thorough research of classic literature and is of bibliographical interest to the artist and the manufacturer.

Chemists who have not seen Dr. Parker C. McIlhiney's original report on boiled linseed oil will welcome its appearance in Prof. Sabin's book. The part of Dr. McIlhiney's paper on bromine absorption should, however, be supplemented by the more recent investigation of Tolman and Munson on this subject.

The chapter on japans and driers gives important information regarding methods of manufacture and effect of these little-known compounds, and will aid the analyst by guiding him along certain lines of investigation.

The theory of baked japan and varnish and its application to metal protection is of interest to the engineer, as is also the vital necessity of thoroughly cleaning all metal surfaces before the coating is applied.

Though the author states it would be useless to give schemes for chemical analysis, due to changes in methods of manufacture and lack of chemical knowledge along the requisite lines, it is to be regretted that Prof. Sabin, with his wide experience as a chemist and manufacturer, has not given more information regarding the constitution and constants of the resin gums, and the changes which occur in the varnish pot.

This is the line of investigation which is of especial interest to the technical chemist, and one which has been given but limited space in chemical literature.

The book is very readable, is clear and concise, with evidence of the author's dry humor and pleasant personality, and is very free from typographical errors. S. S. VOORHEES.

ELEMENTARY MANUAL FOR THE CHEMICAL LABORATORY. By LOUIS WARNER RIGGS, PH.D. New York: John Wiley and Sons. 1904. vi + 138 pp. Price, $1.25.

This manual is "the author's attempt to answer the much debated questions: What subjects shall be taught and how shall they be presented in a one-year course in chemistry"? It is assumed "that there shall be at least sixty hours of recitation work and one hundred and twenty hours of laboratory practice."

Forty-two pages are allotted to general chemistry, including the study of twelve non-metals and five metals with some of their compounds. Thirty-nine pages contain more than thirty exercises in volumetric analysis, while qualitative analysis is taught in fifty-two pages. The complete gravimetric analysis of crystallized magnesium sulphate is the only one of its kind. The book not only contains directions for laboratory practice, but indicates, also, under the rubric, "Text-book Lesson," the topics which the student is expected to prepare for recitation, by studying any "large-sized standard text-book." The modern theory of solution is brought early to the attention of the student and its teachings are followed consistently. It is clear that mastery of the work laid out in this manual will insure the acquisition of more chemistry than one can usually crowd into a one-year course, but it is not so evident that the questions, which led to its preparation, have been satisfactorily answered. L. B. HALL.

A LABORATORY MANUAL OF ORGANIC CHEMISTRY FOR BEGINNERS. By PROFESSOR DR. A. F. HOLLEMAN. Translation from the Dutch by DR. A. JAMIESON WALKER. New York: John Wiley and Sons. xiv + 78 pp. Price, $1.00.

This book was originally written as a practical complement to the lectures on organic chemistry given in the Universities of the Netherlands. It contains concise directions for more than three hundred experiments to illustrate properties, reactions, and general principles connected with the chemistry of the more important carbon compounds. It is a comprehensive introductory guide to laboratory work for the general student, and not essentially a handbook of "Organic Preparations." The experimental directions, although in a few instances less detailed than might be desired, are usually clear and sufficiently definite to be easily

followed by the beginner. Many of the experiments are suitable for the purposes of lecture illustration. The experiments follow the order of the text of the author's well-known "Text-book of Organic Chemistry" that has also been lately made accessible to English readers by the same translator and publishers. The "Laboratory Manual," whether used as intended by its author as an appendix to his "Text-book," or employed as a source of material to supplement the laboratory work in more specialized courses in "Organic Preparations," will doubtless meet a want in this translation, as it has in the original. S. P. MULLIKEN.

EXPERIMENTS ARRANGED FOR STUDENTS IN GENERAL CHEMISTRY. By EDGAR F. SMITH AND HARRY F. KELLER. Fifth Edition. Phila.: P. Blakiston's Son and Co. 94 pp., interleaved. Price, 60 cents.

This is one of the very few laboratory manuals for beginners in chemistry which attempt to illustrate the principles as well as the descriptive side of the subject, and to provide the basis for a really thorough and serious study of the science in both of these directions. The value of a set of laboratory exercises can be judged only by actual use and the fact that this book has reached its fifth, revised, edition shows that the authors have achieved an unusually successful solution of the problem. Teachers who are not already familiar with the work should not fail to examine it seriously. ALEX. SMITH.

CORRECTIONS.

In the paper by Andrew A. Blair on the "Bismuthate Method for the Determination of Manganese":

Page 798, lines 18 and 19, read: "The proportion is 280 : 55 or 1 : 0.19643," instead of "56 : 55 or 1 : 0.98214."

In the foot-note, read 279.5 : 55 or 1 : 0.1968.

In the Alcohometric Tables by E. W. Morley:

Page 1189, the sp. gr. of alcohol of 47 per cent. at 22° should be 0.91892 instead of 0.91992.

Page 1190, the sp. gr. of alcohol of 82 per cent. at 16° should be 0.84199 instead of 0.84189.

Page 1191, the sp. gr. of alcohol of 74 per cent. at 22° should be 0.85641 instead of 0.85621.

Page 1193, line 3 of text, read 0.00010 instead of 0.0010.

Copies of Professor Morley's Alcohometric tables, printed on heavy paper, may be obtained of the Librarian or Editor at ten cents each. Stamps will be accepted.

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